New strategy for the in situ synthesis of single-crystalline MnWO$_4$/TiO$_2$ photocatalysts for efficient and cyclic photodegradation of organic pollutants†

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MnWO$_4$ nano photocatalysts with plate shapes and in high yields are in situ synthesized on the surface of a porous TiO$_2$ film by the conventional plasma electrolytic oxidation (PEO) method combined with a subsequent ambient annealing process. Transmission electron microscopy (TEM) analysis shows that the MnWO$_4$ nano photocatalysts are single crystals free of structural defects and scanning electron microscopy (SEM) observation on the cross-section reveals that these MnWO$_4$ nano photocatalysts are in situ grown on the porous TiO$_2$ film surface with strong adhesion. The morphology and dimension size can be selectively tailored through controlling the reaction time, showing the simplicity and versatility of the proposed method. In addition, the photodegradation of methylene blue (MB) solution using the MnWO$_4$/TiO$_2$ photocatalysts demonstrated the superior photocatalytic performance with high efficiency and excellent photostability. A high photodegradation rate of MB solution of over 90% in 60 min has been achieved and a superior cyclic capability is also obtained. The superior photocatalytic performance of MnWO$_4$/TiO$_2$ photocatalysts can be mainly attributed to the good crystallinity, all-surface covering and strong mechanical properties of the MnWO$_4$ nanostructures with TiO$_2$ film. The prevailing advantage of the PEO method in combination with the ambient annealing process will open up more opportunity for the rational synthesis of a wide range of oxide photocatalysts ranging from tungstate to titanate, molybdate and vanadate for promising catalytic applications in diverse fields.

Introduction

Water is a fundamental requirement for the survival of life and any contamination can pose a threat to survival. It is roughly estimated that half of the total population of the world lacks the availability of clean and sanitized water.$^{1,2}$ One of the major contributors to water pollution is organic waste originating from either industrial, household or individual disposal. A continuous increase in organic waste contaminants in water resources causes a series of health problems for mankind and also has threatened the existence and development of other living beings. Furthermore, organic pollutants with intense carcinogenesis, teratogenesis and mutagenesis endanger human health.$^{3,4}$ The situation becomes even more critical due to the marginal efficiency of traditional sewage biological treatment for organic waste removal.$^{5,6}$ Consequently, it becomes an urgent necessity to search for an efficient technology to remove/degrade organic pollutants from water sources.

Over the past decades, photocatalytic degradation of organic pollutants using catalytically active nanostructures has been demonstrated to be an effective and feasible way towards the purification of contaminated water.$^{7-12}$ Based on this principle, diverse semiconductor nanostructures have been explored. For example, titanium dioxide (TiO$_2$) is most widely used because of its high photocatalytic capability, excellent chemical stability, low cost, non-toxic nature and environmental friendliness.$^{13}$ However, its large band gap (3.2 eV) can only allow for excitation by ultraviolet irradiation which accounts for about 3–4% of solar energy.$^{14,15}$ For this reason, it is worthwhile exploring and fabricating some novel active photocatalysts with a band gap corresponding to efficient visible light absorption for the purpose of fast and efficient photodegradation. Interesting attempts have been reported to overcome the above mentioned problem by using various inorganic photocatalysts such as metal oxides (TiO$_2$,
Bi₄WO₁₂, ZnO, etc.) and metal sulfides (ZnIn₂S₄, CdS, etc.). Among them, manganese tungstate (MnWO₄), with a band gap of 2.65–2.8 eV, has been regarded as a promising catalyst for organic compound degradation due to its suitable band gap, strong redox capability, high photocatalytic efficiency and low cost. Consequently, many researchers have paid much attention to the photocatalytic activity of MnWO₄ prepared by various methods such as the sol-gel method, hydrothermal method, microwave-assisted method, molten salt method, and so on. However, an overwhelming drawback of these MnWO₄ products is that the majority of the as-synthesized materials are in the form of a nano-sized powder, which is a difficulty associated with recovering dispersions of the catalyst for recycling and future use after the photocatalytic reaction. In fact, one of the key factors for the degradation of organic pollutants in water is the separation and recovery of photocatalysts from water. To effectively recycle catalysts, one strategy that has been developed is to prepare nanostructured catalysts on substrates, such as ITO glass and/or metal foil. These structured materials such as the photocatalysts confined on a substrate can be easily separated from water for recycling purposes. On the other hand, the combination of MnWO₄ with some oxide semiconductors (for example TiO₂) to form a heterostructure will also promote the separation of photogenerated electrons and holes. As a result, the improvement of the photo-degradation performance of MnWO₄ nanostructures can be expected.

To address this problem, it has been deduced that macroscale photocatalysts with nanostructures on the substrate may have great potential application in photocatalysis, due to their superior photocatalytic activity, efficient visible light response, low cost and easy cyclic characteristics. Inspired by this, it is desirable to in situ grow MnWO₄ photocatalysts on a solid substrate to maintain their strong mechanical adhesion for repeated use. For this point, plasma electrolytic oxidation (PEO) technology provides a large possibility of achieving such objectives for the reason that it can in situ produce porous TiO₂ films strongly adhered to the surface of the Ti metal by a high voltage discharge in aqueous solution. Simultaneously, various reactant ions in the electrolyte also deposit into the porous TiO₂ film during the PEO process, which can be used as precursors for photocatalyst nucleation and crystallization in a subsequent annealing process, as demonstrated in Ni-Ti-O whiskers. Meanwhile, a heterojunction between MnWO₄ nanostructures and porous TiO₂ films can also be obtained for the realization of enhanced photodegradation capability. Hence, in this work we demonstrate that a large yield of crystalline MnWO₄ nano photocatalysts with controllable morphology and dimensional size can be in situ grown on a porous TiO₂ film surface using conventional PEO technology and an annealing process. Typically, the MnWO₄/TiO₂ photocatalysts with excellent mechanical adhesion present extremely high performance for degrading methylene blue (MB) solution under visible light. The dependence of the morphology and size evolution of these MnWO₄ photocatalysts on annealing time is also systematically investigated. The tentative growth mechanism describing the formation process of the MnWO₄/TiO₂ photocatalysts is proposed.

**Experimental**

**Preparation of MnWO₄/TiO₂ photocatalysts**

To synthesize the MnWO₄/TiO₂ photocatalysts, porous TiO₂ films are first produced on the surface of commercially available titanium plates (grade I, dimensions of 10 mm × 10 mm × 1 mm, Shansi Baotai Group) via the PEO method. The Ti plates are ground to remove the oxide layer and contaminated surface by sandpaper (#2000), and ultrasonically cleaned in ethanol and deionized water for 5 min, respectively. In a typical PEO experiment, the Ti plate is connected to the positive pole of a power supply as the anode and a conductive graphite electrode is linked with the negative pole as the cathode. A schematic diagram of the experimental set-up can be found in the ESI. In a typical PEO experiment, the Ti plate is connected to the positive pole of a power supply as the anode and a conductive graphite electrode is linked with the negative pole as the cathode. A schematic diagram of the experimental set-up can be found in the ESI. Fig. S1. Aqueous solutions comprising of 0.8 mol L⁻¹ Na₃PO₄·12H₂O, 0.04 mol L⁻¹ Na₂B₄O₇·10H₂O, 0.02 mol L⁻¹ Na₂WO₄·2H₂O and 0.1 mol L⁻¹ Mn(CH₂COO)₂·2H₂O are employed as the electrolytes for producing discharge and the subsequent porous PEO film (TiO₂). The optimized PEO time is fixed at 15 min and the applied current density is set at 0.1 A cm⁻². The working frequency is fixed as 1000 Hz. During the PEO process, the electrolyte temperature is controlled below 35 °C to enable a uniform coating formation by adjusting the cooling water flow. After the formation of the porous TiO₂ film, it is immediately transferred to a resistance furnace for annealing at 850 °C at ambient pressure. During this stage, low-dimensional MnWO₄ nanostructures with diverse morphologies can nucleate and crystallize on the surface of the porous TiO₂ film. A schematic description of the formation process of the MnWO₄/TiO₂ photocatalysts can be found in Scheme 1.

**Characterization of the photocatalysts**

X-ray diffraction (XRD, Rigaku D/max 2400) is used to examine the phases and structures of the as-synthesized porous TiO₂ film and MnWO₄ photocatalysts. The XRD patterns are recorded in the 2θ range of 20–60° using Cu Kα (λ = 0.154056 nm) as the X-ray source. Field emission scanning electron microscopy (SEM, FEI Inspect F50) equipped with energy dispersive X-ray spectrometry (EDS, Quanta 600) are employed for morphology observations and composition analysis. The surface composition and the valence state of the as-synthesized photocatalysts are acquired using X-ray photoelectron spectroscopy (XPS, Thermal VG/ESCALAB250). The microstructure and crystallinity analyses of the as-synthesized photocatalysts are carried out using field emission transmission electron microscopy (TEM Tecnai F20) under an accelerated beam voltage of 200 kV.
Photocatalytic test

The evaluation of the photocatalytic performance of the MnWO4/TiO2 photocatalysts is carried out in a 100 mL annular quartz photochemical reactor and MB aqueous solution with an initial concentration of 20 mg L⁻¹ is used as the target organic pollutant. A 300 W xenon lamp equipped with a UV cut-off filter (λ > 400 nm) is used as the excitation source for the photocatalytic reaction and the optical power density is fixed at 150 mW cm⁻². UV-vis spectrophotometry (U-3900, HITACHI, Japan) is used to record the absorptivity of the aqueous solution.

Results and discussion

To synthesize MnWO4/TiO2 photocatalysts and realize their strong adhesion on a solid substrate for cyclic photocatalysis utilization, it is essential to first obtain a high quality porous TiO2 film, which serves as the storage medium for the precursors to form MnWO4 and the underneath layer for forming the heterojunction. A porous TiO2 film with uniform three-dimensional frameworks is in situ generated on the surface of the pure Ti plate through the energetic electrical sparks by the PEO method (Fig. S2†). The typical morphology of the porous TiO2 film with a pore size in the range of 100 nm–5 μm can be seen. XRD measurement confirms that the porous film is TiO2 with a mixed anatase phase and rutile phase (Fig. S3a†). Meanwhile, some amorphous phases are also detected in the TiO2 film and they can be assigned to some W- or Mn-containing compounds due to the drastic temperature gradient produced by the plasma discharge. During the formation of the TiO2 film, ions such as Mn²⁺ and WO₄²⁻ in the electrolyte will be simultaneously deposited/adsorbed in the porous matrix layer as dopants (Mn and W elements) under the effect of electrophoresis and arc discharge (Fig. S3b†). These ions incorporated into the porous TiO2 film are used as the precursors for MnWO4 formation in the subsequent annealing. After the PEO process, an annealing process in ambient air is required to induce the nucleation and crystallization of the MnWO4 photocatalysts on the surface of the porous TiO2 film through a solid-diffusion reaction at a temperature of 850 °C for 60 min. In this stage, the Mn and W elements stored in the porous film will migrate into the film surface and react with ambient oxygen to lead to the formation of MnWO4 nanostructures. With a continuous supply of Mn and W precursors, nanosized MnWO4 with a featured plate-like morphology and the MnWO4/TiO2 photocatalysts can be obtained.

Fig. 1 shows the optical micrographs of the porous TiO2 film after the PEO process and the MnWO4/TiO2 photocatalysts after high temperature annealing at 850 °C. An obvious colour contrast in the appearance of the TiO2 film before and after annealing can be found. Typically, the porous TiO2 film exhibits an obvious dark brown appearance, whereas the colour changes to dark yellow after annealing, as seen in Fig. 1a. An observation of the morphology of the annealed film verifies that the surface of the porous TiO2 film has been densely covered with a large amount of one-dimensional plates with an average length of up to 10 μm (Fig. 1b). Further observation under high magnification shows that the top layer nanostructures hold a faceted rectangle configuration, as highlighted in Fig. 1c. The faceted crystalline edges imply that these plates may have a good crystallinity, which is extremely important for efficient separation of the photo-generated electrons and holes toward improved photocatalytic performance. Different from the photocatalysts prepared by the sol–gel or hydrothermal routines,37,38 which normally aggregate together, the faceted plates are solidly attached on the porous TiO2 film and protrude upward randomly, with overwhelming surfaces exposed outside, which in turn leads to a significant surface area enhancement of the fiber catalysts for excellent photocatalytic performance. Fig. 1d shows the cross-section back-scattering image of the nanoplates on the porous TiO2 film. Obviously, two phases from the plates and the porous film can be clearly observed and their boundary is also apparent, as marked by the yellow dashed line. Phase analysis using XRD verifies that the plates densely grown on the surface of the porous film are MnWO4 (Fig. 1e). Meanwhile, it can be seen that the anatase TiO2 phase has been completely transformed into the rutile TiO2 phase. Composition analysis using EDS measurement further confirms that the plates are composed of Mn, W and O elements with a stoichiometric ratio approaching Mn:W:O = 1:1:4, as shown in Fig. S4.†

In order to investigate the formation of MnWO4 nanostructures, it is essential to examine the chemical states of the TiO2 film and the as-synthesized MnWO4/TiO2
photocatalysts. Fig. 2 shows the XPS spectra of the Mn, W, O and Ti elements for the TiO$_2$ film before and after annealing at 850 °C for 60 min. The entire interpretations of the four elements are extracted based on the C1s core level with a binding energy of 284.6 eV. It can be seen that the Mn 2p curve with doublet peaks at the binding energies of 640.8 eV and 652.6 eV can be attributed to Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$, respectively, as shown in Fig. 2a. No shift of the doublet peaks before and after annealing indicates that the chemical state of Mn does not change. These two peaks correspond to a divalent oxidation state (Mn$^{2+}$) in Mn-containing compounds.\textsuperscript{39} It should be noted that Mn can be adsorbed by the anodic electrical field under the effect of bobble creation and turbulent conditions of the electrolyte in the PEO process.\textsuperscript{40} For the W 4f spectrum (Fig. 2b), it can be seen that the spectrum can be divided into two main peaks (B and C) and two satellite peaks (A and D) for the TiO$_2$ film, similar to previous reports.\textsuperscript{41} Peaks A and B at binding energies of 34.7 eV and 36.8 eV, which correspond to W 4f$_{7/2}$ and W 4f$_{5/2}$, can be attributed to a W$^{6+}$ chemical valance. The energy gap between the two peaks is around 2.1 eV, in good coherence with the reference value of W$^{6+}$.\textsuperscript{42} In addition, the peaks C and D at the binding energies of 36.5 eV and 38.6 eV are allocated to the W$^{4+}$ valance.\textsuperscript{43} The co-emergence of W$^{4+}$ and W$^{6+}$ in the TiO$_2$ film implies that some W$^{6+}$ valances in the electrolyte (WO$_4^{2-}$) have been converted to a lower oxidation state (W$^{4+}$). It has been reported that a stoichiometric ion exchange between W$^{4+}$ and Ti$^{4+}$ can take place because they have a similar ion radius and chemical bond length for W–O and Ti–O.\textsuperscript{44} Furthermore, both WO$_2$ and TiO$_2$ possess the same crystal structures, and the W element can partly replace the Ti sites in the TiO$_2$ lattice.\textsuperscript{43,45} During the formation of the TiO$_2$ film, the high surface temperature and the high applied voltage can promote ion exchange between W$^{4+}$ and Ti$^{4+}$. In combination with the XRD and EDS results, it can be concluded that the MnWO$_4$ phase may have been generated during the PEO process and some W atoms have dispersed into the TiO$_2$ lattice through an ion exchange reaction, further validating our assertion on the formation of an amorphous MnWO$_4$ phase during this stage. After annealing, the peak corresponding to the W$^{4+}$ oxidation state has disappeared, suggesting that the W ions (W$^{4+}$) doped into the TiO$_2$ lattice have escaped and the W$^{4+}$ valance is transformed into the higher valence W$^{6+}$ state subject to the high temperature reaction. Fig. 2c shows the XPS curve of the O1s core level binding energy, and the broad peak can be decomposed to four distinct peaks by Gauss fitting. According to the literature,\textsuperscript{46} the peak corresponding to a binding energy of 532.3 eV can be attributed to the oxygen in water molecules. It can be easily understood that some water molecules will be adsorbed...
on the surface of the TiO₂ film during its formation in aqueous solution. The peak with a binding energy of 531.4 eV represents the hydroxyl groups because the free surface of the oxide material is usually hydrated in the atmosphere. The peak with its maximum energy centered at 530.5 eV corresponds to O²⁻ in MnWO₄, whereas the peak with its binding energy located at 529.6 eV matches well with the oxygen in TiO₂. After annealing, the peak related to oxygen in water attached on the surface of the porous TiO₂ film disappears, indicating that the water molecules have evaporated from the porous TiO₂ film. The binding energy of Ti 2p₃/₂ at 458.4 eV confirms the existence of TiO₂, and the same curve configuration of Ti 2p for the TiO₂ film before and after annealing indicates that the chemical valence of the Ti element has not changed even after high temperature treatment, as shown in Fig. 2d. The evolution of W and O valances after annealing, together with the composition results in Fig. 1e, S3 and S4,† clearly verifies that the MnWO₄ phase has been formed during the high temperature reaction.

To examine the detailed structural characteristics of the MnWO₄ nanoplates, atomically-resolved TEM analysis on dozens of MnWO₄ nanoplates is carried out. Fig. 3a shows a low magnification TEM image of wire-like MnWO₄ nanostructures where the smooth side surface can be clearly observed, in good agreement with the faceted morphology observed in the SEM images in Fig. 1c. High resolution TEM (HRTEM) analyses performed on several randomly selected nanoplates confirm that these MnWO₄ nanostructures annealed at 850 °C have a decent crystallinity. Fig. 3b shows the typical atomically-resolved lattice fringe image of the MnWO₄ nanoplate shown in Fig. 3a. The lattice distances between two adjacent lattice planes parallel and perpendicular to the growth direction are measured to be 0.50 nm and 0.37 nm, respectively, which match well with the d-spacing of the (001) and (110) planes of the wolframite-type monoclinic MnWO₄ structure. Further careful HRTEM investigations on these MnWO₄ nanoplates confirm that no structural defects such as twin or stacking faults can be found, demonstrating again their superior crystal quality. The excellent crystallinity of the MnWO₄ nanoplates also proves the advantage of PEO technology in the control of crystal quality, prevailing to other conventional synthetic routines such as the hydrothermal and sol-gel methods. The defect-free crystallinity of the MnWO₄ nanoplates also paves a solid way for efficient separation of photogenerated electrons and holes in a photocatalytic process. The selected area electron diffraction (SAED) pattern with clearly separated and periodic diffraction spots, as shown in Fig. 3c, further verifies that the as-synthesized MnWO₄ nanoplates are single crystals free of structural defects. Based on the HRTEM image and SAED pattern, the oriented growth direction of the MnWO₄ nanoplate can be determined to be parallel to its c-axis, implying that the MnWO₄ nanoplates prefer to grow along the c-axis due to their anisotropy in a monoclinic structure.²⁰,⁴⁷ From the crystallographic unit structure of monoclinic MnWO₄ with a P2₁/c space group (Fig. 3d), one can see that [MnO₆] and [WO₆] octahedral unit cells share edge form zigzag chains along the c-axis, and tungsten atoms and manganese atoms are arranged in alternating sheets parallel to the (001) plane. Therefore, it may lead to a one-dimensional structure for MnWO₄ crystals because of the intrinsic preferential growth.

Considering that some impurity elements such as W and P have been detected from the TiO₂ film, it is necessary to further check the compositional purity of the MnWO₄ nanoplates. As an example, Fig. 3e shows the representative EDS spectrum collected from the sample nanoplates. It can be seen that only Mn, W, O and Cu elements appear in the spectrum, whereas the P element is not detected. The absence of the P element in the MnWO₄ nanoplates can be assigned to the high temperature annealing process, which removes the P impurity from the TiO₂ film as exhausts. It is reasonable

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Fig. 3  (a) TEM image of MnWO₄ nanoplates; (b) HRTEM image; (c) the corresponding SAED pattern; (d) schematic crystal structure of MnWO₄; (e) the EDS spectrum of the corresponding nanoplate; (f) the dark field image and the corresponding mapping results; (g) EDS intensity profiles of Mn, W and O elements along the radial direction.
to understand that Mn, W, and O peaks with predominant intensities come from the samples, while the Cu signal is produced from the Cu TEM grid, as verified in the EDS spectrum of most nanostructures. The atomic molar ratios among the Mn, W, and O elements detected from the nanoplates can be further roughly quantified to Mn : W : O = 1 : 1 : 4.3, which is close to the stoichiometric ratio of the MnWO₄ crystal. Combined with HRTEM data, it can be confirmed again that the as-synthesized nanoplates are of the pure MnWO₄ phase. Different from other methods like hydrothermal technology, which produces MnWO₄ nanostructures with apparent contaminations like hydroxyl groups attached on the surface, the MnWO₄ nanoplates synthesized by the PEO method exhibit extremely high purity. Fig. 3f shows the spatially-resolved mapping of the Mn, W and O elements inside the MnWO₄ nanoplates. It can be seen that all the elements have a homogeneous distribution. The line-scan profiles of the three elements further demonstrate the composition uniformity of the MnWO₄ nanoplates (Fig. 3g).

Our previous studies have clearly demonstrated that the catalytic performance of the photocatalysts is strongly dependent on their size. To reveal the size–property relationship, time-dependent annealing experiments at 850 °C are carefully carried out. Fig. 4 shows the representative morphologies of the MnWO₄ nanoplates with a duration time of 10, 30, 60 and 240 min at 850 °C, respectively. An obvious evolution of the MnWO₄ nanoplates in size, dimension and growth density can be found. Typically, the 10 min growth leads to the appearance of MnWO₄ nanoplates with a large growth density and a short length of about 1 μm, densely covering the surface of the porous TiO₂ film (Fig. 4a). The magnified SEM image shown in Fig. 4b reveals that rectangle-like crystallographic facets have been developed in this stage. The thickness of the MnWO₄ nanoplates counted from the SEM image is in the range of 100–500 nm. A further increase of the annealing time to 30 min will induce the continuous growth of the MnWO₄ nanoplates along their axial direction with a maximum length of up to 5 μm, corresponding to a crystallization rate of ~200 nm min⁻¹. However, the prolongation of the reaction time will not promote the formation of new nucleation and the size increase in lateral directions (Fig. 4c and d). The same phenomenon in size development as a dependence of reaction time for the MnWO₄ nanoplates is also observed in the case of 60 min growth, as shown in Fig. 4e and f. In this stage, plate-like MnWO₄ nanoplates with uniform morphology and geometrical features can be obtained. The length of the MnWO₄ nanoplates can be up to ~20 μm whereas their thickness still remains at ~200 nm. When the annealing time is extended to 240 min, the MnWO₄ nanoplates show a quite different morphology and size evolution behavior in comparison with the previous ones. Notably, a significant change in plate thickness and width of the MnWO₄ nanoplates has been observed and the size distributions cover a wider range. The width can approach ~5 μm and the thickness can be up to the micrometer scale. In addition, the growth density of the MnWO₄ nanoplates after 240 min growth has sharply decreased compared with that for 60 min growth, and it is found that some huge MnWO₄ nanoplates are mixed with a large fraction of smaller ones. The length prolongation and size expansion of the MnWO₄ nanoplates does not follow the linear propagation with the reaction time. It is reasonable to understand that the formation of the MnWO₄ nanoplates derives from the thermal diffusion reaction and the Mn and W atoms directly come from the precursors initially incorporated in the porous TiO₂ film during the PEO process. At the growth stage from 10–60 min, the Mn and W elements stored in the porous TiO₂ film are sufficient to allow for continuous growth of the MnWO₄ nanoplates and thus a gradient morphology evolution in length can be observed. When the precursors accumulated in the porous film are depleted, no extra Mn and W ions can be transported to the growth frontier of the

Fig. 4 SEM surface morphology of the MnWO₄ nanoplates fabricated for different growth times: (a and b) 10 min; (c and d) 30 min; (e and f) 60 min; and (g and h) 240 min.
MnWO₄ nanoplates and their growth along the axial direction will terminate.

The above results have clearly demonstrated that the PEO method is extremely effective at producing in situ nanostructured MnWO₄ nanoplates with good crystal quality and a tailored morphology on the TiO₂ film surface, showing predominant advantages in comparison with other conventional routines. As schematically described in Scheme 1, the synthesis of the MnWO₄ photocatalysts includes two separated processes. Based on the detailed results in the microstructure and chemical composition analysis, a tentative growth mechanism describing the formation process of the MnWO₄/TiO₂ photocatalysts is proposed. First, the porous TiO₂ film is in situ formed on the Ti substrate under highly energetic discharge. During the formation of the TiO₂ film, the Mn²⁺ and WO₄³⁻ in the electrolyte solutions will be simultaneously incorporated into the porous TiO₂ film. Meanwhile, a tiny amount of Mn-containing amorphous phase may also be produced, as evidenced by the broad dome in the XRD pattern (Fig. S3a†). These Mn²⁺ and WO₄³⁻ ions stored in the porous TiO₂ film are the key precursors for the nucleation and crystallization of the MnWO₄ nanostructures. When the porous TiO₂ film is annealed at 850 °C at ambient pressure, the Mn²⁺ and WO₄³⁻ adsorbed on the surface of the porous TiO₂ film will first nucleate to some nano islands and serve as the seeds for the following growth. The orientation of the plate-like MnWO₄ nanostructures is related to its own intrinsic crystallographic feature and the monoclinic MnWO₄ crystal is constructed by the stacking of octahedral periodic WO₆ and MnO₆ units along the c-axis, as illustrated in Fig. 3d. During the nucleation and crystallization processes, tungsten and manganese atoms will alternatively occupy the planar crystal-line sites parallel to the (001) facets and thereby lead to the preferred orientation along the [001] direction, as reported in one-dimensional tungstate nanostructures with wolframate-type structures.⁴⁸ It should be also noted that some smaller nano islands can also evolve into large ones due to their different solubility according to the Gibbles–Thomos law.⁴⁹ Following this step and with the prolongation of reaction time, these MnWO₄ nano islands will gradually crystallize and the Mn and W elements incorporated into the porous TiO₂ film will diffuse into the TiO₂ film surface along the porous channels to supply stable precursors, and finally develop into plate-like crystals with smooth facets and lead to the formation of the MnWO₄/TiO₂ photocatalysts.

The previous literature has demonstrated that pure MnWO₄ photocatalysts can convert organic pollutants into environmentally friendly compounds under visible light irradiation.²⁰,⁵⁰ To evaluate the photocatalytic performance of the MnWO₄/TiO₂ photocatalysts, the optical properties of the porous TiO₂ film and MnWO₄/TiO₂ photocatalysts annealed at 850 °C for 60 min are separately studied using an UV-vis spectrometer, as shown in Fig. 5. It can be seen that the absorption edges of the porous TiO₂ film and MnWO₄/TiO₂ photocatalysts are located at about 380 nm and 460 nm, respectively. This finding indicates that the MnWO₄/TiO₂ photocatalyst is a visible light-driven photocatalyst, whereas the TiO₂ film (PEO coating) can only be excited by UV light. The band gap of the MnWO₄/TiO₂ photocatalysts can be further estimated to be 2.7 eV through the equation $a h ν = A (h ν - E_g)^{2/3}$, where $\alpha$ denotes the absorption coefficient, $h ν$ is the photon energy, $A$ is a constant, and $E_g$ is the band gap energy. In this case, it should be noted that the absorption mainly comes from the top MnWO₄ nanostructures. The band gap of the MnWO₄ nanostructures is also in good agreement with the reported value.⁵¹ The lower band gap of the MnWO₄/TiO₂ photocatalysts suggests that they are very favorable catalysts for the photodegradation of organic pollution under visible light.

Fig. 6 shows the photodegradation test of the MB aqueous solution using the MnWO₄/TiO₂ photocatalysts and their cyclic performance. In order to disclose the effect of the porous TiO₂ film on the photocatalysis test, the photocatalytic performance of the pure TiO₂ sample, which is prepared under the same experimental parameters without the involvement of the Mn(CH₃COO)₂ precursor in the electrolyte, is also measured. Fig. 6a shows the photocatalytic degradation curves of the MB aqueous solution as a dependence of irradiation time for the pure TiO₂ film and all the MnWO₄/TiO₂ photocatalysts with different morphologies (Fig. 4). Obviously, the blank MB solution shows a low self-degradation rate under irradiation. When the porous TiO₂ film is used, the degradation rate of the MB solution slightly increases and the C/C₀ ratio can only be up to 60% even under an irradiation time as long as 180 min. However, in the case of the MnWO₄/TiO₂ photocatalysts, the photodegradation of the MB aqueous solution exhibits a faster rate with a sharp slope of C/C₀ vs. irradiation time. Especially, the photocatalysts show excellent performance in decomposing the MB solution in the first 60 min and almost 90% of the MB solution can be degraded. The corresponding colour change of the MB solution from being initially blue to transparent further demonstrates the excellent photocatalytic activity of the MnWO₄/TiO₂ photocatalysts (Fig. 6a, inset). Compared with some other popular photocatalysts,⁵²,⁵³ the
MnWO₄/TiO₂ photocatalysts also show a decent performance. Among all the samples, the photocatalysts grown at 850 °C for 60 min present the best performance in decomposing the MB solution, whereas the others with different annealing times of 10 min, 30 min, and 240 min are relatively less active. The difference of photocatalytic capability of these samples can be understood by the morphology characteristic shown in Fig. 4. It can be found that the catalysts with 60 min growth possess a longer length and a large surface area. Therefore, more active sites responsible for the photocatalytic reactions on the surface of the MnWO₄/TiO₂ photocatalysts can be expected. As a result, a superior photodegradation performance of the MnWO₄/TiO₂ photocatalysts with 60 min growth can be achieved.

From the viewpoint of practical application, normally a stable catalytic performance and cyclic utilization of the photocatalysts in pollutant solution are generally required, on the basis of a superior photodegradation capability. To evaluate the possibility of the MnWO₄/TiO₂ photocatalysts for cyclic utilization, the photocatalysts with 60 min growth are tested under the same photocatalytic conditions as those in Fig. 6a and are shown in Fig. 6b. One can see first that the curves show quite a similar resemblance with that in Fig. 6a (60 min). Second, the photodegradation rate and catalytic activity of the MnWO₄/TiO₂ photocatalysts for four cyclic tests almost stay the same, suggesting that the MnWO₄/TiO₂ photocatalysts have excellent photostability. The excellent photocatalytic capability and long-time reusability of the MnWO₄/TiO₂ photocatalyst make it a competitive candidate for practical environmental processing.

Based on the photocatalytic experiment and the reported band gap of MnWO₄ and TiO₂, a tentative photocatalytic mechanism of the MnWO₄/TiO₂ photocatalysts is proposed, as illustrated in Fig. 7. Due to the difference of band potentials between MnWO₄ and TiO₂, it will lead to the generation of an inner electric field at the interface in both of them.

When the photocatalysts are irradiated with visible light, the holes in the valence band (VB) of MnWO₄ will transfer to the VB of TiO₂, and the electrons will drop from the conduction band (CB) of TiO₂ to the CB of MnWO₄. The transference migration of electrons and holes between MnWO₄ and TiO₂ will lead to the effective charge separation of electron–hole pairs. Finally, the photogenerated holes with powerful oxidative radicals will move to the photocatalyst surface and oxidize MB. Meanwhile, the transferred electrons in MnWO₄ with strong reduction capability will be trapped by the adsorbed O₂ molecules to yield ˙O₂⁻ which will decompose MB into CO₂ and H₂O.

Different from powder-type photocatalysts, which exhibit obvious disadvantages in particle aggregation and collection, the MnWO₄/TiO₂ photocatalysts fabricated by the PEO method are firmly confined on the Ti substrate and cannot aggregate together to lead to the decrease of their surface-to-volume areas. Most importantly, there is no quantity/mass loss during the photodegradation process due to the strong adhesion with the substrate, overcoming the predominant
hurdles of powder-based photocatalysts prepared by the hydrothermal or sol–gel methods. These peculiar characteristics of the MnWO$_4$/TiO$_2$ photocatalysts, together with the advantages of the PEO method, allow for their repeated utilization and hold promising potential towards a practical application in organic pollutant processing.

Conclusions

In summary, a new routine toward the rational synthesis of MnWO$_4$/TiO$_2$ photocatalysts with superior crystallinity and excellent photodegradation performance has been developed. The synthetic routine involves the first step PEO process in electrolyte solution to form a porous TiO$_2$ film and a subsequent ambient annealing process for the nucleation and crystallization of MnWO$_4$ nanostructures on it. The morphology, size and nucleation densities of the photocatalysts can be easily tailored through controlling the growth parameters like the reaction time. The photodegradation test using MB as a target organic solution demonstrates that the MnWO$_4$/TiO$_2$ photocatalysts with decent crystallinity and huge surface areas show excellent performance and have promising application potential in decomposing organic pollutants. Cyclic photodegradation performance tests further verify the high efficiency and desirable stability of the MnWO$_4$/TiO$_2$ photocatalysts for their repeated utilization and negligible material depletion, showing predominant advantages in comparison with powder photocatalysts.

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Notes and references