Construction of TiO$_2$–MnO$_2$ 0D–2D nanostructured heterojunction for enhanced photocatalytic hydrogen production†

Guojing Wang, Tao Chen, Shuo Liu, Fengqi Wang, Mingyang Li, Mingzheng Xie, Jing Wang, Yunjie Xiang and Weihua Han

The low transfer efficiency and high recombination loss of photo-induced carriers in TiO$_2$ are significant issues that hinder its photocatalytic activity. Herein, TiO$_2$ nanoparticles (~5 nm) were loaded on MnO$_2$ nanosheets (40–60 nm) to form TiO$_2$–MnO$_2$ nanostructured heterojunction (0D–2D nanostructure unit), possessing a high specific surface area. The separation/transfer efficiency of photocarriers and the solar absorptivity of TiO$_2$–MnO$_2$ were improved, thus enhancing solar energy conversion efficiency. The enhanced transfer efficiency of carriers is associated with the 2D network of MnO$_2$ and abundant oxygen vacancies serving as media for electron transport. The enhanced visible absorption and reduced recombination should be attributed to the narrowed bandgap and modified energy band structure. The photo-current of TiO$_2$–MnO$_2$ increased obviously and the H$_2$ production rate increased to 0.38 mmol g$^{-1}$ h$^{-1}$, compared with that of pure TiO$_2$ (0.25 mmol g$^{-1}$ h$^{-1}$). The enhanced photocatalytic properties are also associated with the excellent water oxidation kinetics caused by MnO$_2$ nanosheets.

1. Introduction

Along with the rapid development of the economy and society, environmental pollution and the energy crisis have become two serious problems facing human beings.$^{1–4}$ It is significant to develop high-performance photocatalytic materials which have the capability of water-splitting or pollutant degradation with solar light.$^{1–5}$ As a commonly used photocatalyst, titanium dioxide (TiO$_2$) has considerable advantages, including being cost-effective, chemically stable, non-toxic, and environmentally friendly.$^{6–9}$ However, there are still unresolved issues that hinder its actual applications. Most of all, TiO$_2$ can only absorb and utilize the ultraviolet (UV) light, which contributes only ~4% of the solar spectrum, due to its wide bandgap (~3.2 eV for anatase TiO$_2$; ~3.0 eV for rutile TiO$_2$).$^{10,11}$ Moreover, the recombination rate of photo-induced electron–hole pairs is too high. This limits photocarriers that can transfer to the photocatalyst surface and react with target molecules in electrolyte.$^{12,13}$ Thus, to break through the bottleneck in light utilization and charge transfer, a lot of efforts have been devoted to changing this situation, including doping TiO$_2$ with impurities,$^{4}$ construction of heterojunction,$^{15}$ surface sensitization by organic dyes,$^{16}$ and modulation of morphology, crystal structure and defects.$^{17–20}$ Among these strategies, the construction of heterojunction is the most attractive and promising one.

Heterojunctions combine their intrinsic characteristics and enhance properties to satisfy newfangled intricate requirements on progressive applications such as heterogeneous photocatalysts.$^{21–24}$ Recently, transition metal oxide photocatalysts have received attention because of their promising performance and low cost.$^{25}$ Manganese oxides (γ-MnO$_2$, β-MnO$_2$, λ-MnO$_2$, α-MnO$_2$, Mn$_3$O$_4$, MnO$_2$ nanomaterials) have good electrocatalytic activity.$^{25–27}$ Considering their variety of types, different crystalline structures, low cost, environmental friendliness and safety, manganese oxides can help to improve the performance of catalytic activity in promoting oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) as well.$^{28,29}$ Manganese oxides (MnO$_2$) have recently emerged in the degradation of organic or inorganic pollutants, as reported in recent literature.$^{30}$ Several synthetic procedures have been
reported to obtain the TiO$_2$–MnO$_2$ nanocomposites for enhancing the photocatalytic activity by increasing the utilization rate of solar energy due to its narrow bandgap, negatively charged surface and large surface area.$^{6,7,10,31}$

Moreover, the two-dimensional (2D) oxide is an ideal supporter to load one-dimensional (1D) and zero-dimensional (0D) nanomaterials, owing to its large contact area and efficient electron-conducting network.$^{32-40}$ MnO$_2$ nanosheet is a promising material for electrochemical energy storage, electrocatalysis and photocatalysis.$^{31,42}$ In this work, TiO$_2$–MnO$_2$ nanostructure with an architecture of nanoparticles ($\sim$5 nm) on nanosheet (40–60 nm) heterojunction (0D–2D) was suggested to heighten the photocatalytic capacity of TiO$_2$. And the main purpose of this research is to enhance the photocatalytic performance of TiO$_2$ by improving the utilization rate of solar energy, specific surface area and mobility of electrons.

2. Experimentation

TiO$_2$–MnO$_2$ heterojunction was assembled using MnO$_2$ nanosheets and TiO$_2$ nanoparticles synthesized by a facile aqueous solution method. Briefly, TiO$_2$ nanoparticles were prepared by a classical sol–gel approach and the preparation technique can refer to our previous work.$^{43,44}$ The MnO$_2$ nanosheets were synthesized by the chemical co-deposition process. The aqueous solution, including MnO$_2$ powder (0.16 g), was ultrasonically treated for 0.5 h and then TiO$_2$ powder (0.25 g) was added to the aqueous solution. This mixed solution was ultrasonically treated for 1 h. The mixture was then dried at 80 °C, following by heat treatment at 300 °C for 4 h. The obtained nanocomposite was TiO$_2$–MnO$_2$. The details of synthesis, characterization, photoelectrochemical measurements and photocatalytic activity evaluation were provided as ESI.$^{†}$

3. Results and discussion

The transmission electron microscopy (TEM) and high resolution (HR) TEM images of bare TiO$_2$ nanoparticles used in this work were displayed in Fig. 1(a) and (b). The size of the TiO$_2$ nanoparticles with a preferred orientation of [001] is around 5 nm. The morphology of MnO$_2$ with a two-dimensional (2D) nanosheet was shown in Fig. 1(c). The diameter of the bare MnO$_2$ nanosheets is about 60 nm and the thickness is around three atoms thick (as shown in Fig. 1(d), HRTEM, marked by red dotted line). After TiO$_2$ nanoparticles were decorated on the MnO$_2$ nanosheets and heated for 4 h, the surface morphology of samples changed significantly, as seen in Fig. 1(e) and Fig. S1(a).† The diameter of MnO$_2$ nanosheets becomes small and is around 40 nm. Compared with the morphology of bare MnO$_2$ (Fig. 1(c)), the decrease in nanosheets’ size after TiO$_2$ loading indicates a well interaction between the TiO$_2$ and MnO$_2$. The clear crystal structure observed in the HRTEM image (Fig. 1(f) and Fig. S1(b))† suggests that the crystallinity of TiO$_2$ and MnO$_2$ is improved (both bare TiO$_2$ and MnO$_2$ show the amorphous structure as illustrated by X-ray diffraction (XRD)). It is clearly seen that there are two kinds of crystal structures. The larger crystal parameter around 0.42 nm is attributed to akhtenskite MnO$_2$ (JCPDS no. 30-0820), which is pale and most of which is observed on edge. The smaller crystal parameter is around 0.24 nm which is belonged to the (004) plane of TiO$_2$ with anatase phase (JCPDS no. 21-1272). Fig. 1(g) is the schematic diagram of TiO$_2$–MnO$_2$. The crystal structure of TiO$_2$ nanoparticles, which show an anatase crystal structure, was verified by the XRD measurements (as shown in Fig. S2†). The MnO$_2$ nanosheets show a pure akhtenskite crystal structure and the weak diffraction peaks of MnO$_2$ indicate the nanosheets are amorphous. The TiO$_2$–MnO$_2$ nanocomposite is observed to be made up of two phases (TiO$_2$ and MnO$_2$). The powders’ structural features were further detected by laser-excited Raman measurements and the results were presented in Fig. 1(h). The Raman spec-
trum of TiO₂ reveals that a major sharp peak at 152.04 cm⁻¹ attributed to the E_g mode of TiO₂ with anatase phase.⁴⁵,⁴⁶ Moreover, the three minor peaks around at 399, 519, and 641 cm⁻¹ are attributed to the B_{3g}, A_{1g}, and E_g vibrational modes of TiO₂ with anatase phase, respectively.⁴⁵,⁴⁶ For the Raman spectrum of MnO₂, a strong peak at 646.84 cm⁻¹ and a minor band at around 579 cm⁻¹ are excited by the scattering of different phonons and Mn–O lattice vibrations of MnO₂.⁵⁹ The Raman spectrum confirms the TiO₂ and MnO₂ composition of the TiO₂–MnO₂ nanocomposites.

In order to investigate the interaction between TiO₂ and MnO₂, some other characterizations were also provided, such as X-ray photoelectron spectroscopy (XPS) measurement. Fig. 2(a)–(c) display the O 1s, Ti 2p, and Mn 2p XPS spectra of MnO₂, TiO₂, and TiO₂–MnO₂. The O 1s spectra of samples are deconvoluted into three peaks: high, middle and low binding energy peak at around 530, 531, and 533 eV, respectively. And they are designated as OH, OM and OL, respectively. Generally, lattice oxygen atoms and oxygen vacancies are responsible for OL and OM peaks, respectively.¹⁹,⁵⁰ The peak at high binding energy is attributed to chemisorbed oxygen due to hydroxyl groups related to chemisorbed water.⁵¹ Obviously, the areas of peaks represented lattice oxygen atoms and oxygen vacancies of MnO₂, TiO₂, and TiO₂–MnO₂ are clearly different. In order to obtain accurate information of the peak, the O 1s spectra of samples were fitted using three Gaussian peaks. Base on the peak areas, ratios of oxygen vacancies/lattice oxygen atoms (Oₐ/Oₐ) were evaluated to be 0.05, 1.51, and 1.42 for TiO₂, MnO₂ and TiO₂–MnO₂, respectively. In addition, the peak position of Ti 2p for TiO₂–MnO₂ shifts to lower binding energy (Fig. 2(b)) compared with TiO₂. Comparing with bare MnO₂, the peak position of Mn 2p for TiO₂–MnO₂ shows no noticeable shift (as shown in Fig. 2(c)). The increment of the electron density of Ti atom in TiO₂–MnO₂ may be attributed to electron transfer via oxygen vacancies on the surface of MnO₂ nanosheets. This conjecture can also be verified by the spectra of O 1s XPS (as shown in Fig. 2(a)). The results of XPS indicate a stable interaction between MnO₂ and TiO₂ via oxygen vacancies. In addition, the atomic ratio of Mn and Ti was identified to be 65.85 : 34.15.

The light-harvesting ability of the samples was characterized by UV-visible absorption spectroscopy. Due to the wide bandgap, the absorption band edge of TiO₂ was observed at 380 nm (as shown in Fig. S3(a)), which means poor absorption of sunlight in the visible region.¹⁰ The TiO₂–MnO₂ nanocomposite shows enhanced absorption in the visible region attributing to the narrow bandgap of MnO₂. The optical bandgap of semiconductor materials can be estimated by Kubelka–Munk function as follows:

\[
(\alpha h\nu)^n = A(h\nu - E_g)
\]

where \(\alpha\) represents absorption coefficient of the material, \(h\nu\) represents incident photon energy, \(n\) represents power factor of transition mode, \(A\) represents a constant termed as the parameter of band tailing and \(E_g\) represents optical bandgap. Because both TiO₂ and MnO₂ are the direct bandgap semiconductor materials, the value of \(n\) is 2. Fig. S3(b) illustrates the linear extrapolation of Tauc plots of TiO₂ and MnO₂ to evaluate the optical bandgap. The optical bandgap of TiO₂ and MnO₂ were determined to be 3.13 and 2.32 eV, respectively.

H₂ production activity of the samples was characterized under simulated sunlight illumination (Fig. 3(a)). The efficiencies of H₂ production of TiO₂ and TiO₂–MnO₂ are about 0.25 mmol g⁻¹ h⁻¹ and 0.38 mmol g⁻¹ h⁻¹, respectively. However, in the same conditions, MnO₂ photocatalyst exhibits no detectable activity due to a lower minimum energy level of the conduction band. Thus, more photo-induced carriers on the TiO₂ conduction band \((E_{CB})\) of TiO₂–MnO₂ nanocomposite are possible. This may result from that TiO₂–MnO₂ nanocomposite is the direct Z-scheme junction (the recombination between the photo-induced electrons located in the conduction band of MnO₂ and the photo-induced holes located in the value band of TiO₂) or the photo-induced electrons located in conduction band transfer from MnO₂ to TiO₂. In addition, a steady increase was observed in the H₂ production of samples with irradiation time increasing. And the activity of the H₂ production didn’t show remarkable inactivation after three cycles (Fig. 3(b)). The results of photocatalytic H₂ production indicate that stable structure and reaction process were formed in TiO₂–MnO₂ nanocomposite photocatalyst.

In order to clarify the transfer path of photo-induced carriers, the diagrams of the energy band structure of TiO₂ and MnO₂ were studied by UPS. Fig. 4(a) illustrates the UPS spectra and the Fermi levels \((E_{FB})\) of TiO₂ and MnO₂ were estimated to

![Image](48x118 to 284x347)
be 2.05 and 4.49 eV, respectively. The maximum energy levels of the valence band ($E_{\text{VB}}$) of TiO$_2$ and MnO$_2$ have been deduced to be 2.08 eV and 1.33 eV lower than the Fermi levels, respectively. The work functions of TiO$_2$ and MnO$_2$ were measured to be around 6.81 and 7.42 eV, respectively. According to the UV-visible absorption spectra, the optical bandgaps of TiO$_2$ and MnO$_2$ are taken as 3.13 and 2.32 eV, respectively. The diagrams of the energy band structure of TiO$_2$ and MnO$_2$ were given in Fig. 4(b). The energy levels of semiconductors can be calculated by empirical equations as follows:

$$E_{\text{CB}} = x - E_e - 0.5E_g$$  \hspace{1cm} (2)

$$E_{\text{VB}} = E_{\text{CB}} + E_g$$  \hspace{1cm} (3)

where $E_{\text{CB}}$ is the potential of conduction band (CB), $E_{\text{VB}}$ is the potential of valence band (VB), $\chi$ is the electronegativity of semiconductor, $E_e$ is the energy of free electrons vs. hydrogen (4.5 eV)$^{51}$ and $E_g$ is the optical bandgap. Moreover, $\chi$ can be calculated using the following equation:

$$\chi = \frac{[\chi(A)^a \chi(B)^b \chi(C)^c]^{1/(a+b+c)}}{a+b+c}$$  \hspace{1cm} (4)

where $a$, $b$, and $c$ are the number of atoms in the semiconductor.$^{54}$ The value of $\chi$ for TiO$_2$ is 5.81 eV. The values of $E_{\text{CB}}$ and $E_{\text{VB}}$ for TiO$_2$ were estimated to be $-0.26$ eV and 2.87 eV versus normal hydrogen electrode (NHE). The value of $\chi$ for MnO$_2$ is 5.96 eV. The values of $E_{\text{CB}}$ and $E_{\text{VB}}$ for MnO$_2$ were estimated to be 0.30 eV and 2.62 eV versus NHE. When TiO$_2$ and MnO$_2$ were assembled together, the Fermi level of the nanocomposite is leveled with the energy band bending at the interface. According to the energy band structure of TiO$_2$ and MnO$_2$, the energy band structure of the nanocomposite and the photo-induced carriers transfer path were displayed in Fig. 4(c). At the interface of the nanocomposite, there formed a potential well on the minimum energy level of CB at the interface that can collect photo-induced electrons. The photo-induced holes located in VB will be transferred from TiO$_2$ to MnO$_2$. This is beneficial for reducing the recombination rate of the photo-induced carriers in the photocatalyst. Thus, the photocatalytic performance of TiO$_2$–MnO$_2$ has been improved.

In order to further estimate the ability of electron transport, the electrical impedance spectra (EIS) of TiO$_2$ and TiO$_2$–MnO$_2$ were investigated. Fig. 5(a) displays the Nyquist curves of TiO$_2$ and TiO$_2$–MnO$_2$ electrodes. Notably, the semidiameter of the curve of TiO$_2$–MnO$_2$ is much smaller than that of TiO$_2$, meaning a lower charge transfer resistance of nano-composite.$^{55}$ For more information, the Nyquist plots of TiO$_2$–MnO$_2$ displays in Fig. 5(b), showing two semicircular arcs. A circuit model of the series connection of a resistor ($R$) and two parallel units (resistor and capacitor, RC) were used to fit the experimental curves (as displayed in the inset of Fig. 5(a)). Table 1 listed the fitted parameters of each of these com-

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**Fig. 3** The performance of photocatalytic H$_2$ production for MnO$_2$, TiO$_2$, and TiO$_2$–MnO$_2$ (a) and the cycling measurement of H$_2$ production of TiO$_2$–MnO$_2$ (b).

**Fig. 4** Typical spectra of He (l) ($h\nu = 21.22$ eV) UPS of TiO$_2$ and MnO$_2$ carried out with $-10.0$ V bias applied on the samples (c). The diagrams of the energy band structure of TiO$_2$ and MnO$_2$ (d). Schematic illustration of TiO$_2$–MnO$_2$ heterojunction charge transfer mechanism (e).

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**Fig. 5** Photoelectrochemical properties of TiO$_2$ and TiO$_2$–MnO$_2$ working electrode. (a) Nyquist curves of TiO$_2$ and TiO$_2$–MnO$_2$ under dark. The solid lines are the fitting results. (b) The Nyquist curve of TiO$_2$–MnO$_2$ under dark. (c) LSV plots of TiO$_2$ and TiO$_2$–MnO$_2$. (d) Transient photocurrent responses for TiO$_2$ and TiO$_2$–MnO$_2$ under the irradiation of simulated solar light.
ponents. These results also indicate that the TiO$_2$–MnO$_2$ nanostructure possesses a fast interfacial charge transfer. The linear sweep voltammograms (LSV) were measured in a three-electrode configuration. Fig. 5(c) shows the LSV characters of TiO$_2$ and TiO$_2$–MnO$_2$ under dark and in simulated sunlight. The TiO$_2$–MnO$_2$ delivers better optoelectronic performance as expected (Fig. 5(c)). The LSV plots of TiO$_2$–MnO$_2$ between 0.75–1.50 V exhibit two oxidation peaks. The first peak, around 1.00 V, corresponds to the formation of MnO$_2$ and the second peak is resulting from the oxygen evolution reaction. Under a 1.5 V vs. Ag/AgCl, TiO$_2$ shows a very low photocurrent of $\sim$0.50 mA cm$^{-2}$, indicating the photo-induced carriers at the surface of TiO$_2$ give rise to severe recombination. However, the photocurrent density of TiO$_2$–MnO$_2$ powder is 8.73 mA cm$^{-2}$ at the same potential, indicating an obviously improved photocurrent. Perhaps the reason for this is that the nanostructure heterogeneity and abundant oxygen vacancies facilitate the transport of carriers. This is partly attributed to the expanded light absorption range and enhanced light absorption ability. In addition, the TiO$_2$–MnO$_2$ nanocomposite presents a large dark current (Fig. 5(c)) due to the excellent performance of oxygen evolution reaction and the more reactive sites for redox reaction caused by the higher specific surface area of TiO$_2$–MnO$_2$. Fig. 5(d) exhibits the transient photocurrent response of electrodes under the simulated sunlight irradiation (carried out at $\sim$0.6 V vs. Ag/AgCl). Upon irradiation, the intensity of the current of electrodes increases rapidly; on the contrary, the intensity of current reduces instantaneously when the lamp was off. This fast response to illumination implies that the change carriers transmit very quickly in the sample. Usually, the volt ampere characteristic curves of MnO$_2$ exhibit two oxidation peaks between 0.30–1.85 V, without illumination. Therefore, TiO$_2$–MnO$_2$ electrode has a large dark current. It is worth noting that TiO$_2$–MnO$_2$ electrode has a higher difference between the photocurrent density and dark current density than that of TiO$_2$ electrode, verifying the less charge recombi-
nation of photo-induced carriers, the fast photo-induced carriers transport and the enhanced photoelectric response of the nanocomposite electrodes.

In addition, the photogenerated electron lifetime ($\tau_e$) of TiO$_2$ and TiO$_2$–MnO$_2$ can be determined from the EIS Bode-phase plots. The photogenerated electron lifetime of semiconductors can be calculated by empirical equations as follows:

$$\tau_e = 1/2\pi f_{max}$$

where $\tau_e$ is the photogenerated electron lifetime of semiconductors, $f_{max}$ is the frequency that the low-frequency peak appears. Fig. 6 shows the EIS Bode-phase plots of TiO$_2$ and TiO$_2$–MnO$_2$. The $f_{max}$ of TiO$_2$ is 1.78 Hz. The $f_{max}$ of TiO$_2$–MnO$_2$ is much lower than that of TiO$_2$ and thus $f_{max}$ exceeds the measurement range. This means that the photogenerated electron lifetime of TiO$_2$–MnO$_2$ is much longer than that of TiO$_2$.

According to the aforementioned analytic results, the mechanism for the improved photocatalytic performance of TiO$_2$–MnO$_2$ has been revealed as follows:

1. The enhanced water oxidation kinetics of TiO$_2$–MnO$_2$ was due to the excellent electrochemistry properties of MnO$_2$ nanosheets.
2. The interfacial charge transfer could be improved, which is associated with the nanostructure heterogeneity and abundant oxygen vacancies serving as media for electron transport.
3. The energy band structure of the nanocomposite is beneficial to reduce the recombination rate of the photo-induced carriers.
4. TiO$_2$–MnO$_2$ shows a stronger absorption in the visible wavelengths resulting from the narrow bandgap of MnO$_2$.

### 4. Conclusions

In conclusion, the TiO$_2$–MnO$_2$ 0D–2D nanostructure heterojunction was synthesized by the aqueous solution method. The TiO$_2$ nanoparticles (~5 nm) with anatase phase were loaded on akhtenskite MnO$_2$ nanosheets (40–60 nm). Compared with TiO$_2$ nanoparticles, the electrical impedance of TiO$_2$–MnO$_2$ nanocomposite was obviously decreased, which is mainly attributed to the nanostructure heterostructure formation and abundant oxygen vacancies that facilitate the transport of carriers. The efficiencies of H$_2$ production of TiO$_2$ and TiO$_2$–MnO$_2$ are 0.25 and 0.38 mmol g$^{-1}$ h$^{-1}$, respectively.
The improved photocatalytic performance is attributed to the enhanced absorption in the visible wavelengths, the fast charge transfer and the excellent water oxidation kinetics caused by MnO2 nanosheets. Moreover, the energy band structure of the nanocomposite is beneficial to reduce the recombination rate of the photo-induced carriers.

Author contributions

G. J. Wang designed the study, proposed the mechanism, and wrote the manuscript. G. J. Wang, T. Chen, S. Liu, F. Q. Wang and J. Wang performed the experiments and analyzed the data. M. Y. Li, Y. Xiang, M. Z. Xie and W. H. Han polished the manuscript. All authors reviewed the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

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Notes and references