Solid-State, Low-Cost, and Green Synthesis and Robust Photochemical Hydrogen Evolution Performance of Ternary TiO$_2$/MgTiO$_3$/C Photocatalysts

Zhongmei Yang, Yunhong Jiang, Wei Zhang, ..., Jiuren Yin, Ping Zhang, Hean Luo

HIGHLIGHTS
The synthetic process does not involve any organic solvents and hazardous by-products

The optimal sample shows a $\text{H}_2$ evolution rate of 33.3 mmol·h$^{-1}$·g$^{-1}$ under one sunlight

The optimal sample keeps a $\text{H}_2$ evolution rate of 1.46 mmol·h$^{-1}$·g$^{-1}$ under visible light

Uniform carbon layer was ingeniously deposited on the surface of photocatalysts
Article

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SUMMARY

Solar-driven photochemical hydrogen evolution is a promising route to sustainable hydrogen fuel production. Large-scale preparation of highly active photocatalysts using elementally abundant and less-expensive materials is urgently required for widespread practical application. Here, we report a highly efficient and low-cost TiO$_2$/MgTiO$_3$/C heterostructure photocatalyst for photochemical water splitting, which was synthesized on gram scale via a facile mechanochemical method. The heterostructure and carbon sensitization offer excellent photoconversion efficiency as well as good photostability. Under irradiation of one AM 1.5G sunlight, the optimal TiO$_2$/MgTiO$_3$/C photocatalyst can show a great solar-driven hydrogen evolution rate (33.3 mmol h$^{-1}$ g$^{-1}$), which is much higher than the best yields ever reported for MgTiO$_3$-related photocatalysts or pure TiO$_2$ (P-25). We hope this work will attract more attention to inspire further work by others for the development of low-cost, efficient, and robust photocatalysts for producing hydrogen in artificial photosynthetic systems.

INTRODUCTION

Hydrogen is an ecofriendly and renewable energy resource that has been widely investigated to replace traditional fossil fuels because of its high gravimetric energy density. Photocatalytic water splitting under irradiation by solar light has received intense attention for the production of renewable hydrogen from water on a large scale. Great efforts have been devoted to explore effective strategies to design advanced photocatalytic materials (Tong et al., 2012), with rapid progress achieved since the first proposal of water splitting by Honda and Fujishima using a TiO$_2$ electrode in the early 1970s (Fujishima and Honda, 1972). Photocatalysts play a crucial role for solar-to-hydrogen efficiency by lowering the energetic barriers for reaction as they determine how much photoexcitation occurs in a semiconductor under solar illumination and how many photoexcited carriers reach the surface where water splitting takes place (Hisatomi et al., 2014). Most available water splitting photocatalysts are built using expensive noble metals (such as Pt, Ta, Ru, Ir, and Rh), but for widespread practical applications of photocatalytic hydrogen evolution, one should not only take into account high activity for the photocatalysts but also consider the yield, cost, and environment friendliness. Although new photocatalyst materials for water splitting have recently been developed one after another, very few meet the above requirements, with alternative strategies for the synthesis of cost-effective and highly efficient photocatalytic materials and water splitting still very desirable.

Titanium dioxide (TiO$_2$) is a promising substrate for the photogeneration of hydrogen from water because of its fascinating features such as chemical inertness, photostability, environment lines, and low cost (Schneider et al., 2014). Numerous groups have worked on the optimization and engineering of TiO$_2$-based nanostructures, such as elemental doping, forming hybrid architectures, hydrogenization, and constructing heterostructures including wet-chemical and thermochemical approaches (Chen and Burda, 2008; Chen et al., 2011; Lu et al., 2010). Among these approaches, forming a heterojunction with metals or semiconductors has been demonstrated to promote charge separation and transfer of photogenerated electron and hole pairs, and, consequently, improve photocatalytic H$_2$ generation efficiency (Wang et al., 2014).

Magnesium titanate (MgTiO$_3$), as a member of the perovskite family (such as SrTiO$_3$, BaTiO$_3$, and CaTiO$_3$), has been investigated and employed as a ceramic capacitor and resonator because of its low dielectric loss

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1Institute of Rheological Mechanics, Xiangtan University, Xiangtan, Hunan 411105, P. R. China
2National Engineering Center of Chemical Engineering Process Simulation and Enhancement, Xiangtan University, Xiangtan, Hunan 411105, P. R. China
3These authors contributed equally
4Lead Contact
*Correspondence: yhding@xtu.edu.cn (Y.D.), zhangp@xtu.edu.cn (P.Z.)
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and high thermal stability at high frequencies (Surendran et al., 2008). Owing to the wide band gap of MgTiO3 (3.5 eV), few scientific groups have studied it as a noble photocatalyst. However, based on the previously reported strategy for photocatalytic water splitting, photocatalysts must have suitable energy levels for the conduction band (CB) and valence band (VB), as the bottom of the CB must be located at a more negative potential than the reduction potential of H+/H2 (0 V versus normal hydrogen electrode [NHE]), whereas the top of the VB must exceed the oxidation potential of H2O to O2 (1.23 V versus NHE) (Tachibana et al., 2012). MgTiO3 possesses suitable electronic structures and CB (-1.13 eV) or VB (2.37 eV) positions (Zhang et al., 2016b), which matches well with the redox potential of water into hydrogen and oxygen. Moreover, the bottom of the CB of perovskite photocatalysts mainly consists of empty transition-metal d orbitals (Ti4+) and is located at a potential more negative than 0 V, which has the potential activity for water splitting (Zhang et al., 2016a). Therefore, due to the good flat-band potential and photovoltage, MgTiO3 may lead itself to be a desirable photocatalyst for water splitting.

Nevertheless, both TiO2 and MgTiO3 are wide-band-gap semiconductors, which cover only a small fraction (<4%) of the total solar spectrum reaching the surface of the earth. In response to this issue, it is necessary to extend the absorbance spectrum into the visible light region (≈43%). Carbon materials have rapidly emerged due to the unique properties of conjugated materials for electron transport and photoelectronic coupling ability (Yang et al., 2017). In addition, carbon coating offers the intrinsic properties of being stable, inexpensive, able to cover a broader spectrum range, and environment friendly. Herein, we propose that carbon coating should be an ideal candidate for improving the transport of photocarriers through the formation of electronic interactions with TiO2/MgTiO3 heterostructures. Although the synthesis of carbon-coated photocatalysts and a subsequently enhanced photocatalytic activity have been reported extensively in the literature, the in situ formation of a uniform carbon layer onto the surface of a photocatalyst by ingeniously using nascent carbon atoms has never been reported before. The nascent carbon atoms were produced from the reduction of CO2 by Mg in the calcination process, leading to the formation of the carbon coating.

Synthesis of MgTiO3-related photocatalysts such as MgTiO3/MgTi2O5/TiO2 (Meng et al., 2017), Si/MgTiO3 (Zhu et al., 2016), pure MgTiO3 nanofibers (Wang et al., 2017), and MgTiO3/MgTi2O5 (Qu et al., 2013) has been reported by very few groups, but the photocatalytic efficiency is barely satisfactory. In addition, most of the methods are taken in aqueous solution, and they commonly involve organic solvents and produce hazardous by-products, and furthermore, in most cases, the reaction process is difficult to control and shows a low yield (Yang et al., 2018). If the full potential of the materials is to be realized, it is, thus, highly desirable to devise a large-scale and ecofriendly route with reproducible shape control. In response to this important technological challenge, we propose here a facile solid-state reaction as a means of synthesizing carbon-layer-coated TiO2/MgTiO3 heterostructures in a Mg(OH)2·4MgCO3·5H2O medium at 550°C in the presence of TiO2 and metal Mg, with the as-prepared photocatalysts showing a robust solar light-driven hydrogen evolution performance.

RESULTS AND DISCUSSION

Scheme 1 is the schematic diagram of the preparation process of the TiO2/MgTiO2/C (TMC) samples. In a typical process, nonstoichiometric TiO2, Mg(OH)2·4MgCO3·5H2O, and Mg powder (99.9%) were mixed and ground for 1 h; set weight ratios of 9:1, 7:3, 5:5, and 3:7 for TiO2/MgTiO3 in TMCs were used for the photocatalyst samples, which were labeled as TMC1, TMC2, TMC3, and TMC4, respectively (Table S1).
The obtained samples contain different Ti/Mg atomic ratios, which could be accurately controlled by adjusting the dosage of precursors according to the chemical reaction equation; then the samples were placed in a corundum crucible and inserted into a tubular furnace, annealed at 550°C under Ar atmosphere for 10 h, and subsequently cooled to room temperature. The mixtures were collected, washed several times with 0.1 mol/L HCl solution and ultrapure water, and then vacuum dried at 70°C overnight in a drying oven.

We can easily and routinely scale-up this process to produce grams of TMC heterostructure nanomaterials. All feedstocks were made from elementally abundant and less-expensive materials, with the whole synthetic process not involving the use of any organic solvents and hazardous by-products.

Owing to the heterojunctions, suitable CB/VB positions, and uniform carbon coating, the obtained catalysts exhibited a current density of 0.14 mA cm⁻² without a bias voltage, as well as excellent durability. Consequently, under irradiation by simulated sunlight (power: one sunlight), the TMC2 photocatalyst with a Ti/Mg molar ratio of 4:1 can give a great solar-driven hydrogen evolution rate (33.3 mmol h⁻¹ g⁻¹), which is much higher than the best yields ever reported for MgTiO₃-related photocatalysts or P-25 TiO₂ (Bin Adnan et al., 2018). The evolution of abundant bubbles, which commenced as soon as the sample was irradiated by either artificial or natural sunlight, can be clearly seen in Videos S1 and S2 (See Supplemental Information for details).

The purity and crystallinity of TMC samples were examined by using powder X-ray diffraction (XRD) (Figure 1). Very few, if any, impurity peaks are present. The XRD patterns clearly show mixed diffraction peaks, which can be indexed to the anatase TiO₂ (JCPDS card No. 21–1272) and geikielite MgTiO₃ (JCPDS card No. 06–0494), indicating that MgTiO₃ with a high degree of crystallinity was successfully synthesized by our method. With an increasing amount of Mg source, the intensity of the MgTiO₃ peaks relatively improved, suggesting a different content of MgTiO₃ in the TMC samples. The calculated lattice constants for TiO₂ and MgTiO₃ are in good agreement with standard data, and the variation can be ignored, suggesting that elemental doping does not exist in TMC heterostructure materials (Table S2). Carbon-related peaks were not observed because of the low crystallinity.

To reveal the structure, composition, and surface uniformity of the carbon shell, TMC2 was observed using transmission electron microscopy (TEM) and scanning TEM. Figure 2A presents a low-magnification TEM
image of TMC2, demonstrating a clear amorphous shell on the surface of TiO2/MgTiO3 nanocomposites (painted as red). Figure 2B shows the high-resolution TEM (HRTEM) image of TMC2 from the region 1 in Figure 2A, which identified a high-quality polycrystalline feature for TMC2 with an amorphous coating layer. Obviously, three sets of lattice fringes were measured with a lattice spacing of 0.46, 0.27, and 0.35 nm, matching well with the (003) and (104) planes of geikielite MgTiO3 and (101) planes of anatase TiO2, respectively. As shown in Figure 2A, the continuous lattice fringes can be clearly observed at the interfaces (ellipse regions) between TiO2 and MgTiO3, indicating the formation of heterostructure. In addition, a uniform amorphous coating with a thickness of ≈2.7 nm could be clearly observed, which should be the carbon coating. Figure 2C is the HRTEM image of the region 2 in Figure 2A, in which the lattice spacing of the particle next to TiO2 is 0.27 nm, matching with the (104) planes of geikielite MgTiO3. In Figure 2C, an obvious heterojunction structure can be also found at the interface of the two phases. Figure 2D is the corresponding high-angle annular dark-field image for TMC2 sample taken from the area shown in Figure 2B, which also demonstrates a typical heterostructure nanocomposite based on the different atomic weight. Corresponding elemental mappings (Figures 2E–2H) display the spatial arrangements for the Mg, O, Ti, and C elements in the region, confirming the elemental composition of TMC2. Obviously, C elements exhibited a fairly uniform distribution across the entire nanocomposite, suggesting a carbon shell structure. Note, no Mg signal could be observed in the selective area (circular region) of Figure 2D, indicating that the nanoparticle should be TiO2, which is consistent with the HRTEM result.

X-ray photoelectron spectroscopy (XPS) was performed to clarify the elemental composition and valence states for the TMC sample (Figure S2). The full scan spectrum in Figure S2A confirms that Mg, Ti, O, and C coexist in the sample, in good accordance with the result from TEM-energy-dispersive X-ray spectroscopy (EDX) elemental mapping. The fine XPS spectrum for the C 1s signal (Figure S2B) was well fitted with three contributions, which could be ascribed to C=C (284.6 eV), C-OH (285.6 eV), and C=O (288.4 eV), respectively. No Ti-C bond (281 eV) was observed, suggesting that the carbon element did not dope into the TMC phase. If the carbon element has a doping state, its content must be extremely low. The nature of the carbon existing in TMC2 was also characterized by Raman spectroscopy, with the result shown in Figure S3 confirming the presence of sp2 planar and conjugated structures within the carbon layer of TMC2. As shown in Figure S2C, the binding energy between Ti 2p1/2 (458.5 eV) and Ti 2p3/2 (464.2 eV) is 5.7 eV, which illustrates a normal state of Ti4+ in the sample (Qin et al., 2017). With respect to the high-resolution XPS spectra for O 1s in Figure S2D, the three peaks at 529.7, 530.3, and 531.6 eV were fitted, which should be regarded as Ti-O-Ti (lattice O), Mg-O, and C=O (and COO) species, respectively. The high-resolution XPS spectra for the Mg 1s and Mg 2s are located at 1,304.3 and 89.2 eV (Figures S2E and S2F), respectively, indicating the presence of Mg2+ (Zhang et al., 2016b). The XPS results, especially the high-resolution XPS spectra for Mg and Ti, suggest that MgTiO3 formed with Mg and Ti in valences of +2 and +4, respectively. The XRD, TEM, and XPS results confirmed the composition of TiO2, MgTiO3, and carbon. It should be stressed that the formation of MgTiO3 is due to the calcination process, which was confirmed by the XRD results before heat treatment (Figure S4). After Mg(OH)2·4MgCO3·5H2O was thermally decomposed to MgO and CO2, the products continue to react with TiO2 and Mg to produce MgTiO3 and carbon, respectively. In the post-calcination process, TiO2 and MgTiO3 form heterojunctions and carbon deposits on their surfaces. As the sintering temperature is kept at 550°C, the reaction between MgTiO3 and TiO2 will not continue to produce MgTi2O5, which requires a reaction temperature of more than 1,000°C (Suzuki and Shinoda, 2011). This two-step reaction has been confirmed by the XRD results (Figure 1).

UV-visible diffuse reflectance spectroscopy was employed to characterize the optical properties of TMC serial samples (Figure S5). All samples exhibit enhanced absorption bands from 400 to 800 nm due to the effective light absorption property of the functional carbon coating in TMC nanocomposites. The absorbance was enhanced in sequence from TMC1 to TMC4 with the increase in carbon content. The carbon layer can introduce a sensitization effect to extend the response of TiO2/MgTiO3 heterostructure materials into the visible light range of the solar spectrum. Moreover, a joint electronic state will form at the interface of a TiO2/MgTiO3 core and carbon shell, resulting in a synergistic effect (Sahare et al., 2017).
However, a carbon coating is a double-edged sword: the excessive thickness of a carbon shell will block the absorption of light and decrease the photocatalytic activity to a large extent. In the present work, TMC2 with a carbon coating of 2.7 nm exhibits the best photocatalytic performance, which is consistent with previous reported results, i.e., the optimal thickness for the carbon coating is 1–3 nm (Zhang et al., 2008). In Figure S6, the carbon thickness of TMC1, TMC3, and TMC4 samples was characterized by HRTEM, which was about 1.0, 5.0, and 10 nm, respectively. The thickness of carbon coating is determined by Mg (reductant), Mg(OH)$_2$·4MgCO$_3$·5H$_2$O (carbon source), and the sintering time; it is reasonable that the thickness of carbon coating increases correspondingly with the increasing mass percentage of MgTiO$_3$. In addition, unlike the general carbon layer produced from carbonization of organic species, here, the carbon layer was formed by reducing CO$_2$ gas, so it did not contain organic functional groups, which are derived from incomplete graphitization. These functional groups have been demonstrated to be the recombination center for e$^-$/h$^+$ pairs, leading to a decrease in the photocatalytic property (Jing et al., 2013).

The time evolution for H$_2$ production due to solar-driven water splitting with 0.005 g of TMCs and P-25 TiO$_2$ from a continuous measurement is shown in Figure 3A. The efficiency of the first 2 hours was to be affected by the photodeposition of platinum ions, and then reached peak value at the third hour; the slight decline in performance at the last 2 hours is due to the adverse reaction caused by the generated hydrogen in the test system, or the consumption of sacrificial agents. Different molar ratios for Ti/Mg give different H$_2$ production efficiencies; when the atomic ratio of Ti/Mg $\approx$ 4:1, one reaches the best photocatalytic performance. The rate of hydrogen production is 33.3 mmol·h$^{-1}$·g$^{-1}$, which is much higher than the best yield ever reported for MgTiO$_3$-related photocatalysts or pure TiO$_2$ (Degussa P-25, 7.9 mmol·h$^{-1}$·g$^{-1}$) (Bin Adnan et al., 2018). Besides, it is necessary to compare TMCs with the recent achievements of TiO$_2$-based materials for photocatalytic H$_2$ production. Based on the reported works, such as SrSO$_4$/TiO$_2$/Pt (10.5 mmol·h$^{-1}$·g$^{-1}$) (Wang et al., 2019), Pt$^0$ and oxidized Pt$^{3+}$-modified TiO$_2$ nanosheets (20.88 mmol·h$^{-1}$·g$^{-1}$) (Jin et al., 2017), Bi$_2$O$_3$@TiO$_2$ nanotubes (26.02 mmol·h$^{-1}$·g$^{-1}$) (Lakshmana Reddy et al., 2017), Cu(II) pre-grafted Pt/TiO$_2$ (27.2 mmol·h$^{-1}$·g$^{-1}$) (Doozi et al., 2017), C/TiO$_2$ nanotube/carbon nanotubes (37.6 mmol·h$^{-1}$·g$^{-1}$) (Zhaoh et al., 2014), and Mg-reduced black TiO$_2$ (43 mmol·h$^{-1}$·g$^{-1}$) (Sinha-mahapatra et al., 2015), whether or not the photocatalytic hydrogen production rate of TMC samples is the highest, considering the simplicity, environment friendliness, low-cost, and high yield of the synthesis method, TMC photocatalysts still have great advantages. Figure 3B shows repeated, photocatalytic water splitting experiments for the TMC2 photocatalyst under AM 1.5 G illumination, which exhibits a good durability without a significant drop in activity; even after the fifth cycle (25 h), the hydrogen production efficiency loss is less than 5%. The XRD analysis of TMC2 sample after 25 h of photochemical reaction shows that the compositions and crystal structures of TMC2 do not change (Figure S7). This confirms our previous
assumption that slight performance degradation is due to the consumption of sacrificial agents or the adverse reaction. The photostability result suggests that TMC2 heterostructure materials are promising stable photocatalysts under solar light, which should result from the protection afforded by the uniform carbon coating (Wang et al., 2016).

Scheme 2 depicts the charge separation and transfer over the TMC nanocomposite, which has two different situations in UV and visible light regions. In the UV region, MgTiO3 is excited by the high-energy UV light to produce photogenerated electron-hole pairs. Driven by the internal electric field of the heterojunction, photogenerated electrons are transferred to the CB of TiO2, whereas holes are transferred in the opposite direction, which makes them difficult to recombine. In addition, carbon is a kind of high-work-function material, so the photogenerated electrons are quickly transferred to the reaction sites because of the electrostatic attraction, where carbon coating can trap electrons due to its good conductivity (Pan et al., 2017). Thus the possibility for recombination of e⁻/h⁺ pairs decreases.

Based on the reported works, carbon coating will couple with the undercoordinated Ti atoms to restructure into an optimal structure (Lee et al., 2012); this kind of hybrid effect in TMCs plays an important role in visible light region. Figure 4A shows the hydrogen production performance of TMC2 and P-25 TiO2 under irradiation of AM1.5G or pure visible light. The TMC2 sample could still maintain a hydrogen production efficiency of 1.46 mmol·h⁻¹·g⁻¹ after switching the light source to pure visible light. As comparison, hydrogen production cannot be observed when P-25 TiO2 was used. This result suggests that TMC2 enhances the absorption and utilization of visible light. First, carbon coating is excited by visible light to produce excited state electrons, and then the electrons are injected to the CB of MgTiO3 by the d-π conjugation. Owing to the electric field in the heterojunction, the electrons will continue to transfer to the CB of TiO2 and follow to react with water on the surface. Therefore, the carbon shell enables TMC samples to absorb a high amount of photoenergy in the visible region, effectively driving the photochemical hydrogen evolution reaction.

To understand the correlation between the photoactivity and light absorption, the incident photon to charge carrier generation efficiency (IPCE) of P-25 TiO2 and TMC2 photoanodes were measured at 0.23 V versus Ag/AgCl. The IPCE was calculated according to the following equation (Shi et al., 2018):

\[
\text{IPCE(\%)} = \frac{1240 \times I_{sc}(\text{mA} \cdot \text{cm}^{-2})}{\lambda(\text{nm}) \times I_{inc}(\text{mW} \cdot \text{cm}^{-2})} \times 100
\]

where \(I_{sc}\) is the photocurrent density (mA·cm⁻²) under illumination, \(\lambda\) is the wavelength (nm) of incident radiation, and \(I_{inc}\) is the incident light power intensity on the TMC2 electrode (mW·cm⁻²). Compared with P-25 TiO2, the photoactivity of TMC2 sample in the UV region was significantly enhanced and the IPCE value in the wavelength range from 300 to 370 nm was close to 90% (Figure 4B). It illustrates that the separation and transport efficiency of photoinduced carriers of TMC2 sample under UV irradiation is greatly
improved. In addition, we found that the IPCE value of TMC2 is higher than that of P-25 TiO2 in the visible light region from 400 to 470 nm, which means that TMC2 sample not only has good UV photoelectric conversion efficiency but also can absorb and utilize an amount of visible light.

To evaluate the photocatalytic water splitting activity of TMCs and further illustrate the enhanced electron transfer in samples, the photoelectrochemical properties of TMCs were investigated. Figure 5A shows plots for the transient photocurrent response (TPC) versus time for TMCs without bias voltage, which was carried out under AM 1.5G illumination with several 30-s light on/off cycles. All the four samples show a good photoresponse for chopped-light cycles. The photocurrent values are almost zero without light source, whereas the photocurrent rapidly restores to a steady-state value upon irradiation, which is reproducible for several on/off cycles with almost identical photocurrent and dark current (the evolution of abundant bubbles commenced as soon as the sample was irradiated by light and stopped after the light was cut off, which can be clearly seen in Video S3). TMC2 shows the best steady-state photocurrent (0.14 mA cm$^{-2}$), indicating that a large number of photoinduced carriers are present in TMC2 due to the improved charge separation and a more efficient transfer process from TiO2/MgTiO3 heterojunctions to the carbon shell. Figure 5B shows a set of linear sweeps recorded under AM 1.5 G illumination. The potential was swept linearly at a scan rate of 0.1 V/s between 0.0 and 2.0 V versus Ag/AgCl in 0.5 M Na2SO4 electrolyte (pH = 6.82). Obviously, the photocurrent for TMC2 is distinctly higher than that of the other samples, indicating more efficient separation of the photogenerated e$^-$/h$^+$ pairs in TMC2 at the interfaces, which enables more charge carriers to form reactive species, thereby generating a higher photocurrent response. Moreover, the onset potential for the photocurrent reveals a slight shift from −1.35 V for TMC1 to −1.50 V for TMC2. The higher photocurrent density and lower onset potential indicates more efficient charge separation and transport in the TMC2 (Cui et al., 2014). This result should be attributed to the enhanced visible-light absorption of TMCs that is mainly caused by the photosensitization of the carbon coating, which contributes to the overall photocatalytic performance. The measurement of electrochemical impedance can provide further evidence of carrier separation efficiency in the as-prepared TMC samples. The radius of the semicircle on the electrochemical impedance spectra (EIS) reflects the interface layer resistance at the electrode surface. The smaller arc radius implies higher efficiency for charge transfer (Liu et al., 2016). The Nyquist plots showing the EIS in Figure 5C show that the interfacial resistance for TMC2 is much smaller than the other samples, indicating that charge separation in TMC2 is more efficient. Therefore, we can conclude that charge transfer is facilitated across the interfaces between the TiO2/MgTiO3 heterojunctions and carbon shell. The Mott-Schottky (MT) plots for TMC1 and TMC2 show a positive slope (Figure 5D), characteristic of an n-type semiconductor. The difference in the slopes for the two plots suggests an obvious disparity for the donor
densities in TMC1 and TMC2. Carrier density could be calculated from the slope with the following equation:

\[ N_d = \left( \frac{2}{e_0 \varepsilon_0} \right) \left| \frac{d(1/C^2)}{dV} \right|^{-1} \]

where \( e_0 \) is the electron charge of \( 1.602 \times 10^{-19} \) C, \( \varepsilon \) is the relative permittivity of 31 (for anatase), \( \varepsilon_0 \) is the vacuum permittivity of \( 8.854 \times 10^{-12} \) F·m\(^{-1}\), \( N_d \) is the carrier density, and \( d(1/C^2)/dV \) is the straight slope (Song et al., 2018). The calculated electron densities for TMC1 and TMC2 are \( 4.54 \times 10^{19} \) and \( 3.85 \times 10^{21} \) cm\(^{-3}\), respectively. The electron density for TMC2 is approximately two orders magnitude higher than that for TMC1. This indicates that the nanostructure in ternary TMC composites produces an exponential increase of the electron density due to the heterojunctions at the interfaces. In addition, the expected upward shift of the Fermi level caused by the appropriate carbon shell can lead to a decrease in bending of the band edge at the surface of TMC2, facilitating charge separation at the interface (Narayan et al., 2014). Therefore, the improved charge transport, along with the facilitated charge separation, is

Figure 5. Results of Photoelectrochemical (PEC) Test
(A) Transient photocurrent responses for TiO2/MgTiO3/C samples without bias voltage.
(B) Linear-sweep voltammograms collected under 100 mW·cm\(^{-2}\) illumination using a three-electrode setup (TMCs working, Pt counter, Ag/AgCl reference electrode, scan rate of 0.1 V/s in 0.5 M Na\(_2\)SO\(_4\) electrolyte [pH = 6.82]).
(C) Nyquist plots showing the electrochemical impedance spectra for the TMCs.
(D) Mott-Schottky (MT) plots for TMC1 and TMC2 collected at a frequency of 1 kHz in the dark (the inset image shows a magnified MT plot for TMC1).
responsible for the much more efficient photochemical water splitting. As discussed above, TPC, linear-
sweep voltammograms, EIS, and MT results not only correlate well with each other but also are consistent
with the performance-testing results. We believe that better photocatalytic performance for TMCs could
be achieved by optimizing the Ti/Mg molar ratio and the thickness of the carbon shell.

A photoluminescence (PL) emission test is usually used to evaluate the efficiency of charge carrier trapping,
migration, and transfer in a semiconductor, as lower emission intensity means lower recombination rate for
the charge carriers (Li et al., 2013). Figure 6 shows PL spectra for the TMC samples measured using an exci-
tation wavelength of 325 nm at room temperature; all the samples show a band-edge emission peak
centered at approximately 430 nm in the visible region, which is caused by the recombination of the photo-
induced e−/h+ pairs (Wang et al., 2009). As shown in Figure 6, the band-edge emission intensity for TMC1
is remarkably quenched, indicating the presence of a direct interaction among TiO2, MgTiO3, and the car-
bon layer, which enhances the nonradiative relaxation of excitons formed in TMCs. TMC2 exhibits the lowest
emission intensity, which means an obvious lower recombination rate, i.e., a more efficient separation and
transfer of photogenerated e−/h+ pairs, with the lifetime of the charge carriers effectively lengthened. This is
in accordance with the photoelectrochemical (PEC) and performance-testing results. Therefore, PL results
demonstrate that heterostructures and carbon coating accelerate the separation of e−/h+ pairs and inhibit
the recombination of direct and trap-related charge carriers because the photoinduced electrons can swiftly
transfer to the carbon layer through the heterojunctions, following to react with water to produce hydrogen.

In conclusion, we have synthesized and characterized a stable, robust, and promising material for potential
use in photocatalytic hydrogen production. The optimal sample shows a great hydrogen production rate
(33.3 mmol·h−1·g−1), indicating that TMC heterostructure materials are very effective at separating photo-
induced e−/h+ pairs and strongly inhibiting their recombination. A deep discussion into the mechanism for
improved photocatalytic activity was investigated carefully. We believe this work may open up new insights
to develop large-scale, inexpensive photocatalysts with high solar energy conversion efficiency in artificial
photosynthetic systems.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

Limitations of the Study
The Ti/Mg molar ratio and the thickness of the carbon shell could be optimized, and the modulation of the
exposed facets of the catalyst would be valuable.
SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.03.009.

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AUTHOR CONTRIBUTIONS
Y.D. and P.Z. designed and conceived this work; Z.Y. and Yunhong Jiang contributed equally to this work and carried out the synthesis, characterization, and the catalytic test. W.Z., Yong Jiang, J.Y., and H.L. analyzed the catalytic results. Z.Y. and Y.D. wrote the paper, and all the authors participated in the discussion of the results.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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REFERENCES
Bin Adnan, M.A., Arifin, K., Menggu, L.J., and Kassim, M.B. (2018). Titaniate-based perovskites for photochemical and photoelectrochemical water splitting applications: a review. Int. J. Hydrogen Energy 43, 23209–23220.

Chem. Soc. Rev. 42, 9509–9549.

Chen, X., and Burda, C. (2008). The electronic origin of the visible-light absorption properties of C-, N- and S-doped TiO2 nanomaterials. J. Am. Chem. Soc. 130, 5018–5019.

Growing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. Science 311, 746–750.

Cui, H., Zhao, W., Yang, C., Yin, H., Lin, T., Shan, Y., Xie, Y., Gu, H., and Huang, F. (2014). Black TiO2 nanotube arrays for high-efficiency photoelectrochemical water-splitting. J. Mater. Chem. A 2, 8612–8616.

Dozzi, M.V., Chiarello, G.L., Pedroni, M., Livraghi, S., Gianneli, E., and Selli, E. (2017). High photocatalytic hydrogen production on CuI pre-grafted Pr/TiO2. Appl. Catal. B Environ. 209, 417–428.

Fujishima, A., and Honda, K. (1972). Electrochemical photolysis of water at a semiconductor electrode. Nature 238, 37–38.

Hisatomi, T., Kubota, J., and Domen, K. (2014). Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. Chem. Soc. Rev. 43, 7520–7535.

Jin, J., Wang, C., Ren, X.-N., Huang, S.-Z., Wu, M., Chen, L.-H., Hasan, T., Wang, B.-J., Li, Y., and Su, B.-L. (2017). Anchoring ultralarge metallic and oxidized Pt nanoclusters on yolk-shell TiO2 for unprecedentedly high photocatalytic hydrogen production. Nano Energy 38, 118–126.

Jing, L., Zhou, W., Tian, G., and Fu, H. (2013). Surface tuning for oxide-based nanomaterials as efficient photocatalysts. Chem. Soc. Rev. 42, 9509–9549.

Lee, J.S., You, K.H., and Park, C.B. (2012). Highly photoactive, low bandgap TiO2 nanoparticles wrapped by graphene. Adv. Mater. 24, 1084–1088.

Li, M., Luo, W., Cao, D., Zhao, X., Li, Z., Yu, T., and Zou, Z. (2013). A co-catalyst-loaded Ta3N5 photoanode with a high solar photocurrent for water splitting upon facile removal of the surface layer. Angew. Chem. Int. Ed. 52, 11016–11020.

Liu, G., Zhao, G., Zhou, W., Liu, Y., Pang, H., Zhang, H., Hao, D., Meng, X., Li, P., Kako, T., et al. (2016). In situ bond modulation of graphitic carbon nitride to construct p-n homojunctions for enhanced photocatalytic hydrogen production. Adv. Funct. Mater. 26, 6822–6829.

Lu, X., Huang, F., Mou, X., Wang, Y., and Xu, F. (2010). A general preparation strategy for hybrid TiO2, hierarchical spheres and their enhanced solar energy utilization efficiency. Adv. Mater. 22, 3719–3722.

Meng, L., Ren, Z., Zhou, W., Qu, Y., and Wang, G. (2017). MgTiO3/MgTi2O5 heterogeneous belt-junctions with high photocatalytic hydrogen production activity. Nano Res. 10, 295–304.

Narayan, M.U., Jun, L.W., Min, L.J., Youngtak, O., Young, K.J., Eun, K.J., Jongwon, S., Hee, H.T., and Ouk, K.S. (2014). 25th anniversary article: chemically modified/doped carbon nanotubes & graphene for optimized nanostructures & nanodevices. Adv. Mater. 26, 40–67.

Pan, Y.X., You, Y., Xin, S., Li, Y., Fu, G., Cui, Z., Men, Y.L., Cao, F.F., Yu, S.H., and Goodenough, J.B. (2017). Photocatalytic CO2 reduction by carbon-coated indium-oxide nanobelt. J. Am. Chem. Soc. 139, 4123–4129.

Qin, N., Xiong, J., Liang, R., Liu, Y., Zhang, S., Li, Y., Li, Z., and Wu, L. (2017). Highly efficient photocatalytic H2 evolution over Mo2C/CdS-TiO2 nanofibers prepared by an electrospinning mediated photodeposition method. Appl. Catal. B Environ. 202, 374–380.

Qu, Y., Zhou, W., Xie, Y., Jiang, L., Wang, J., Tian, G., Ren, Z., Tian, C., and Fu, H. (2013). A novel phase-mixed MgTiO3-MgTi2O5 heterogeneous nanorod for high efficiency photocatalytic hydrogen production. Chem. Commun. (Camb.) 49, 8510–8512.

Sahare, S., Ghodereao, P., Dey, A., Datar, S., and Bhave, T. (2017). Study of modification of photoactive material with carbon nanomaterials for polymer solar cell applications. Mater. Today Commun. 12, 11–18.

Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiiuchi, Y., Anpo, M., and Bahnemann, D.W. (2014). Understanding TiO2 photocatalysis: mechanisms and materials. Chem. Rev. 114, 9919–9986.

Shi, X., Ueno, K., Oshikiri, T., Sun, Q., Sasaki, K., and Miasawa, H. (2018). Enhanced water splitting under modald strong coupling conditions. Nat. Nanotechnol. 13, 953–958.

Sinhaiahapatra, A., Jeon, J.-P., and Yu, J.-S. (2015). A new approach to prepare highly active and stable black titania for visible light-assisted
hydrogen production. Energy Environ. Sci. 8, 3539–3544.

Song, X., Li, W., He, D., Wu, H., Ke, Z., Jiang, C., Wang, G., and Xiao, X. (2018). The "Midas Touch" transformation of TiO2 nanowire arrays during visible light photoelectrochemical performance by carbon/nitrogen coimplantation. Adv. Energy Mater. 8, 1800165.

Surendran, K.P., Wu, A., Vilarinho, P.M., and Ferreira, V.M. (2008). Sol-Gel synthesis of low-loss MgTiO3 thin films by a non-methoxyethanol route. Chem. Mater. 20, 4260–4267.

Suzuki, Y., and Shinoda, Y. (2011). Magnesium dititanate (MgTi2O5) with pseudobrookite structure: a review. Sci. Technol. Adv. Mater. 12, 034301.

Tachibana, Y., Vayssieres, L., and Durrant, J.R. (2012). Artificial photosynthesis for solar water-splitting. Nat. Photonics 6, 511.

Tong, H., Ouyang, S., Bi, Y., Umezawa, N., Oshikiri, M., and Ye, J. (2012). Nano-photocatalytic materials: possibilities and challenges. Adv. Mater. 24, 229–251.

Wang, H., Zhang, L., Chen, Z., Hu, J., Li, S., Wang, Z., Liu, J., and Wang, X. (2014). Semiconductor heterojunction photocatalysts: design, construction, and photocatalytic performances. Chem. Soc. Rev. 43, 5234–5244.

Wang, L., Yang, G., Peng, S., Wang, J., Ji, D., Yan, W., and Ramakrishna, S. (2017). Fabrication of MgTiO3 nanofibers by electrospinning and their photocatalytic water splitting activity. Int. J. Hydrogen Energy 42, 25882–25890.

Wang, Q., Hisatomi, T., Jia, Q., Tokudome, H., Zhong, M., Wang, C., Pan, Z., Takata, T., Nakabayashi, M., Shibata, N., et al. (2016). Scalable water splitting on particulate photocatalyst sheets with a solar-to-hydrogen energy conversion efficiency exceeding 1%. Nat. Mater. 15, 611–615.

Wang, X., Maeda, K., Chen, X., Takanabe, K., Domen, K., Hou, Y., Fu, X., and Antonietti, M. (2009). Polymeric semiconductors for artificial photosynthesis: hydrogen evolution by mesoporous graphitic carbon nitride with visible light. J. Am. Chem. Soc. 131, 1680–1681.

Wang, Z., Yang, Q., Liu, W., Ran, H., Zhang, C., Han, X., He, X., Wang, X., and Hu, C. (2019). Optical porous hollow-boxes assembled by SrSO4/TiO2/Pt nanoparticles for high performance of photocatalytic H2 evolution. Nano Energy 59, 129–137.

Yang, G., Wang, L., Zhao, Y., Peng, S., Wang, J., Ji, D., Wang, Z., Yan, W., and Ramakrishna, S. (2018). One-dimensional Mg3TiO5-heterostructures: general synthesis and enhanced photocatalytic performance. Appl. Catal. B Environ. 225, 332–339.

Yang, Z., Jiang, Y., Yu, Q., Ding, Y., Jiang, Y., Yin, J., and Zhang, P. (2017). Facile preparation of exposed (001) facet TiO2 nanobelts coated by monolayer carbon and its high-performance photocatalytic activity. J. Mater. Sci. 52, 13586–13595.

Zhang, G., Liu, G., Wang, L., and Irvine, J.T. (2016a). Inorganic perovskite photocatalysts for solar energy utilization. Chem. Soc. Rev. 45, 5951–5984.

Zhang, L.-W., Fu, H.-B., and Zhu, Y.-F. (2008). Efficient TiO2 photocatalysts from surface hybridization of TiO2 particles with graphite-like carbon. Adv. Funct. Mater. 18, 2180–2189.

Zhang, N., Qu, Y., Pan, K., Wang, G., and Li, Y. (2016b). Synthesis of pure phase Mg2.3Ti1.7O5 and MgTiO3 nanocrystals for photocatalytic hydrogen production. Nano Res. 9, 726–734.

Zhao, C., Luo, H., Chen, F., Zhang, P., Yi, L., and You, K. (2014). A novel composite of TiO2 nanotubes with remarkably high efficiency for hydrogen production in solar-driven water splitting. Energy Environ. Sci. 7, 1700–1707.

Zhu, W., Han, D., Niu, L., Wu, T., and Guan, H. (2016). Z-scheme Si/MgTiO3 porous heterostructures: noble metal and sacrificial agent free photocatalytic hydrogen evolution. Int. J. Hydrogen Energy 41, 14713–14720.
Supplemental Information

Solid-State, Low-Cost, and Green Synthesis
and Robust Photochemical Hydrogen Evolution
Performance of Ternary TiO$_2$/MgTiO$_3$/C Photocatalysts

Zhongmei Yang, Yunhong Jiang, Wei Zhang, Yanhuai Ding, Yong Jiang, Jiuren Yin, Ping Zhang, and Hean Luo
**Figure S1.** The TEM and HRTEM images of a single TiO$_2$/MgTiO$_3$/C nanoparticle, related to Scheme 1. (a) The TEM image of a single TiO$_2$/MgTiO$_3$/C nanoparticle; (b) The corresponding HRTEM image from the black square frame in Fig. S1a, confirming the phase of TiO$_2$, MgTiO$_3$ and carbon coating (painted as red). In Fig. S1b, two sets of lattice fringes were measured with a lattice spacing of 0.27 and 0.35 nm, matching well with the (104) and (101) planes of geikielite MgTiO$_3$ and anatase TiO$_2$, respectively.
Figure S2. The full and high-resolution XPS spectrums of TMC2, related to Figure 2.

(a) The full XPS spectrum. (b) C 1s. (c) Ti 2p. (d) O 1s. (e) Mg 1s. (f) Mg 2s.
**Figure S3.** Raman spectra of TMC2, related to Figure 2. The two intense broad peaks around at 1353.4 and 1589.7 cm\(^{-1}\), which are respectively assigned to the D- and G-band of the carbon layer. The Raman-active E\(_{2g}\) mode at 1589.7 cm\(^{-1}\) is characteristic for graphite-like shell, which confirms the presence of \(sp^2\) planar and conjugated structures within the carbon layer of TMC2. The D-band at around 1353.4 cm\(^{-1}\) can be attributed to the presence of the disordered graphite-like carbon within the hexagonal structure. The I\(_D\)/I\(_G\) ratio is indicative of the quality degree of the carbon coating, the relatively low ratio (\(\sim 0.85\)) means that TMC2 with thinner carbon coating of good contact formed a more ordered carbon structure during the calcination procedure.
Figure S4. XRD patterns of TiO$_2$/MgTiO$_3$/C samples before heat treatment, related to Figure 1. The diffraction peaks could be ascribed to TiO$_2$ (Degussa, P-25) and metal Mg, no peaks belong to MgTiO$_3$, indicating that MgTiO$_3$ was not formed yet after grinding.
Figure S5. UV-vis diffuse reflectance spectra (DRS) of the TMC1, TMC2, TMC3 and TMC4, related to Figure 4b.
Figure S6. The HRTEM images of TMC1, TMC3 and TMC4, related to Figure 2.

The thickness of carbon coating could be observed clearly, confirming different thickness of the carbon coating in TiO\textsubscript{2}/MgTiO\textsubscript{3}/C samples.
**Figure S7.** The XRD pattern of TMC2 sample after the fifth cycle (25 hours), related to Figure 3b. Figure S7 shows that the composition and crystal structure of the TMC2 sample do not change, indicating that the as-prepared photocatalysts have good optical stability. The slight reduction of the performance mainly comes from the consumption of sacrificial agent or the adverse reaction.
**Table S1.** Experimental recipe of TMC series and the corresponding results, related to Figure 2.

| Name | TiO$_2$/MgTiO$_3$ (Weight ratio) | TiO$_2$ (g) | MCB$^i$ (g) | Mg$^i$ (g) | Ti/Mg Atomic ratio$^{ii}$ |
|------|---------------------------------|-------------|-------------|------------|--------------------------|
| TMC1 | 9:1                             | 1.0         | 0.12        | 0.05       | 9:1                      |
| TMC2 | 7:3                             | 1.0         | 0.4         | 0.15       | 4:1                      |
| TMC3 | 5:5                             | 1.0         | 0.6         | 0.24       | 3:1                      |
| TMC4 | 3:7                             | 1.0         | 0.85        | 0.34       | 10:7                     |

MCB: Mg(OH)$_2$·4MgCO$_3$·5H$_2$O; $^i$: determined by the desired addition based on the above reaction formula; $^{ii}$: determined by TEM-EDS;
Table S2. The unit cell parameters of TMC samples calculated by software Jade 6.5, related to Figure 1.

| Name       | TiO$_2$ (a=b, Å) | TiO$_2$ (c, Å) | MgTiO$_3$ (a=b, Å) | MgTiO$_3$ (c, Å) |
|------------|------------------|----------------|--------------------|------------------|
| TMC1       | 3.7862           | 9.5185         | 5.0534             | 13.8934          |
| TMC2       | 3.7826           | 9.5129         | 5.0565             | 13.8974          |
| TMC3       | 3.7823           | 9.5148         | 5.0544             | 13.8940          |
| TMC4       | 3.7856           | 9.5033         | 5.0522             | 13.8951          |
| Anatase TiO$_2$ | 3.7852       | 9.5139         | -                  | -                |
| JCPDS No. 21-1272 |            |                |                    |                  |
| Geikielite MgTiO$_3$ | -            | -              | 5.054              | 13.898           |
| JCPDS No. 06-0694 |            |                |                    |                  |
**Transparent Methods**

**Materials**

Titanium oxide (TiO$_2$, Degussa P-25) were bought from Sinopharm Chemical Reagent Co., Ltd, P. R. China. Magnesium carbonate basic (Mg(OH)$_2$·4MgCO$_3$·5H$_2$O, AR) was purchased from Shanghai Macklin Biochemical Co., Ltd, P. R. China. Magnesium Powder (Mg, 99.9%) was obtained from Shanghai Longxin Technology Development Co., Ltd, P. R. China. Hydrochloric acid (HCl, AR) was purchased from Xilong Scientific Co., Ltd, P. R. China. All materials used in this research were used without further purification. Ultrapure water was used throughout this study.

**Preparation of TiO$_2$/MgTiO$_3$/C heterostructures**

A typical synthesis process was as follows: First, 1.0 g of TiO$_2$ were added to different amount of Mg(OH)$_2$·4MgCO$_3$·5H$_2$O matrix salt and metal Mg (99.9 %) in an agate mortar (The stoichiometric ratio based on the following reaction formula, as shown in Tab. S1), then the mixture was ground for 1 hour at room temperature. Second, the obtained samples were placed in a corundum crucible and inserted into a tubular furnace, annealed at 550 °C under Ar atmosphere for 10 h, and subsequently cooled to room temperature. The mixtures were subjected to ultrasonic washing with 0.1 mol/L HCl and filtration, repeated it for several times until pH < 7 making sure the by-product MgO had been washed off. Then the products were washed with ultrapure water over and over until Cl$^-$ ions cannot be detected and vacuum dried at 70 °C overnight in a drying oven. Based on the different weight ratio of TiO$_2$/MgTiO$_3$ (9:1,
7:3, 5:5, 3:7), the samples were labeled as TMC1, TMC2, TMC3 and TMC4, respectively. The corresponding process conditions are listed in Table S1.

The reaction process can be divided to three steps:

\[
(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O \rightarrow 5MgO + 6H_2O + 4CO_2
\]

\[
TiO_2 + MgO \rightarrow MgTiO_3
\]

\[
CO_2 + 2Mg \rightarrow C + 2MgO
\]

The integral reaction formula can be represented as following:

\[
(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O + 5TiO_2 + 8Mg \rightarrow 5MgTiO_3 + 4C + 8MgO + 6H_2O
\]

**Characterization**

Powder X-ray diffraction (XRD) patterns of the samples were performed at room temperature by a Bruker D8 Advance X-ray diffractometer with Cu Ka (λ = 0.15406 nm). The transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were obtained by using a Tecnai G2 F30 S-TWIN high-resolution transmission electron microscope, using an acceleration voltage of 200 kV. UV-vis diffuse reflectance spectra (DRS) was carried out using a Perkin Elmer Lambda 950 spectrometer equipped with an integrated sphere attachment in the range from 200 to 800 nm. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCA Lab 250 electron spectrometer from VG Scientific using an aluminum Ka X-ray radiation source (h = 1486.6 eV). The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. The photoluminescence (PL) spectra was measured at room temperature on a F-4600 FL
fluorescence spectrophotometer using a 325 nm excitation light. Raman spectroscopy was conducted using a Raman microscope (Renishaw in via microscope equipped with 488 nm Ar ion laser and a grating of 2400 L/mm) with a spectral resolution of < 1 cm\(^{-1}\). The specific surface area (BET) was measured with a 3H-2000PS2 instrument, using the adsorption of N\(_2\) at the temperature of liquid nitrogen.

**Photocatalytic hydrogen production**

Photocatalytic hydrogen production was conducted on an online photocatalytic hydrogen production system (PerfectLight, Beijing, China, Labsolar-ⅢAG). A full spectrum solar simulator (Perfectlight, Beijing, China, PLS-SXE300) with AM 1.5G filter is used as the excitation light source (Power: 1 sun light). A powder sample of the photocatalyst (0.05 g) was suspended in a mixture of 70 mL of ultrapure water and 30 mL of triethanolamine (TEOA) in the cell and treated by ultrasound for 30 min. The distance between lamp and liquid-level was about 10 cm, the irradiation area was 10 cm\(^2\). The whole photocatalytic reaction took place at room temperature. During the photocatalytic process, vigorous magnetic stirring and cooling water were used to help the catalysts perform efficiently and to keep the system at room temperature, respectively. Pt-loaded photocatalysts were prepared by using *in situ* photo-deposition method. On this case, the photocatalyst powder was added to an aqueous TEOA solution containing the required amount (1 wt. % of Pt) of H\(_2\)PtCl\(_6\). The high purity Ar gas at a rate of 6.0 ml·min\(^{-1}\), regulated by a CS200 mass flow controller (Sevenstar, Beijing, China), as a carrier gas, flowed continuously through the reactor and allowed
the hydrogen released by the photocatalytic water splitting under irradiation. The resultant gas flowed through the quantitative loop of a six-way valve to a vent, while it was tested by using gas chromatography (Fuli Instruments, Zhejiang, China, GC9790, thermal conductivity detector (TCD), 5 Å molecular sieve columns and Ar carrier) every 1 h to analyze the hydrogen content so as to determine the hydrogen production rate. The mass flow controllers and gas chromatography were calibrated before each experiment.

**Photo-electrochemical measurements**

Photoelectrochemical measurements (PEC) were performed in three-electrode quartz cells with a 0.5 mol/L Na$_2$SO$_4$ (pH= 6.82) electrolyte solution. Platinum mesh (2 × 3 cm$^2$) was used as the counter electrode, and Ag/AgCl (KCl saturated) were used as the reference electrodes. The working electrode made as: 10 mg of TMC photocatalyst and 10 ml ethanol were mixed under an ultrasonic wave for 10 min to produce a slurry, which was then spin-coated onto a 2 × 3 cm$^2$ ITO glass substrate. The coated layer was dried at 80 °C for 12 h in an electrical oven, then went through 400 °C calcination under Ar atmosphere for 1 h. The photoelectrochemical experiment results were recorded using an electrochemical system (Shanghai Chenhua Instruments, CHI760E). A 300 W Xe lamp (Beijing Perfectlight, PLS-SXE300) equipped with an AM 1.5G filter was used as the light source. Potentials were given with reference to the Ag/AgCl. The photo response of the samples as visible light on and off was measured at 0.0 V. Electrochemical impedance spectra (EIS) were measured at 0.0 V. A
sinusoidal ac perturbation of 5 mV was applied to the electrode over the frequency range from 0.05 to 105 Hz. The Mott-Schottky plots were obtained at a fixed frequency of 1 kHz in the dark.