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Article

Synthesis of core-shell nanostructured $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ for photocatalytic hydrogen production

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ABSTRACT

In this study, the $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ composite was synthesized via the calcination of yolk-shell MIL-101@ TiO_2 . The composite presented core-shell structure, where Cr-doped TiO_2 and $\text{Cr}_2\text{O}_3/\text{C}$ were the shell and core, respectively. The introduction of Cr^{3+} and $\text{Cr}_2\text{O}_3/\text{C}$, which were derived from the calcination of MIL-101, in the composite enhanced its visible light absorbing ability and lowered the recombination rate of the photogenerated electrons and holes. The large surface area of the $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ composite provided numerous active sites for the photoreduction reaction. Consequently, the photocatalytic performance of the composite for the production of H_2 was better than that of pure TiO_2 . Under the irradiation of a 300 W Xe arc lamp, the H_2 production rate of the $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ composite that was calcined at 500 °C was $446 \mu\text{mol h}^{-1} \text{g}^{-1}$, which was approximately four times higher than that of pristine TiO_2 nanoparticles. Moreover, the composite exhibited the high H_2 production rate of $25.5 \mu\text{mol h}^{-1} \text{g}^{-1}$ under visible light irradiation ($\lambda > 420 \text{ nm}$). The high photocatalytic performance of $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ could be attributed to its wide visible light photoreponse range and efficient separation of photogenerated electrons and holes. This paper offers some insights into the design of a novel efficient photocatalyst for water-splitting applications.

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1. Introduction

The amount of sun energy that reaches the earth every second is approximately $1.465 \times 10^{14} \text{ J}$, which is the equivalent of the 10-day workload of a power plant. Although it is difficult to entirely convert solar energy into useful energy, improving energy conversion efficiency is extremely important for the development of mankind. Converting solar energy into H_2 fuel via photocatalysis is considered to be a promising method for alleviating the worsening worldwide energy crisis, and could

also solve the global environmental problems [1–3]. Semiconductor materials have been attracting researchers' attention ever since Fujishima and Honda published their paper on the use of the TiO_2 electrode for splitting water [4]. To date, semiconductor materials (e.g., CuO [5], ZnO [6], SnO_2 [7], graphitic carbon nitride [8–11], CdS [12,13], and BiVO_4 [14,15]) have been used as photocatalysts for photocatalytic H_2 production systems. Compared to other semiconductor photocatalytic materials, TiO_2 is more advantageous owing to its robust chemical stability, low cost, and non-toxicity [16,17]. However, its high

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photogenerated electron-hole pairs recombination rate and low absorption capability for visible light, which was attributed to its wide bandgap (~ 3.2 eV), significantly limit the use of TiO_2 for photocatalytic applications [18].

Many scholars have reported improving the photocatalytic activity of TiO_2 via heteroatom-doping [19], surface modification [20,21], the loading co-catalysts [22–24], and the formation of heterojunctions [25–28]. Among these methods, the transition-metal cation modification of TiO_2 is an effective strategy for enhancing the visible light absorption ability and improving the photocatalytic properties of TiO_2 [29,30]. Cr_2O_3 has been considered to be an efficient visible-light-inducing photocatalytic material owing to its narrow bandgap, and thus, it has been explored as a dopant for TiO_2 [31,32]. Irie et al. [33] doped Cr^{3+} into TiO_2 powder using the impregnation method to improve its photocatalytic properties. Jun and Lee [34] synthesized Cr-doped TiO_2 films and demonstrated that their different band gaps depended on the sputtering parameters. Wang et al. [35] synthesized Cr and Co co-doped crystal TiO_2 powder using the sol-gel method, studied its sonocatalytic activity for the degradation of azo fuchsine, and determined that the sonocatalytic activity of Cr and Co co-doped TiO_2 powder for the degradation of azo fuchsine exceeded that of pristine TiO_2 . All the above-mentioned studies confirmed that Cr doping and Cr_2O_3 modification could improve the photocatalytic activity of TiO_2 .

Metal-organic frameworks (MOFs) have received considerable attention in many research areas owing to their unique structure, which involves high surface areas and numerous micropores [36,37]. Using MOFs as precursors and templates is promising for obtaining porous materials with well-tunable structure and high surface area [38,39]. The high surface area, large porosity, and tailorability of MOFs could be inherited by their derivatives, and therefore, MOFs-derived materials present great potential for catalytic applications. To date, most studies have been focusing on the preparation of porous carbon [40,41], metallic oxide or C/metallic oxide composites [42–44] via the calcination of MOFs under different atmospheres. Using MOF-derived C/metallic oxide porous materials and TiO_2 as cores and shells, respectively, to design novel photocatalysts could be a promising strategy for improving the photocatalytic efficiency of TiO_2 by improving the diffusion efficiency of the reactants and providing more active sites for the catalytic reactions. In this study, $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ composites were successfully prepared using $\text{Cr}_2\text{O}_3/\text{C}$ that was derived from MIL-101 ($\text{Cr}_3\text{O}(\text{OH})(\text{H}_2\text{O})_2[\text{C}_6\text{H}_4(\text{CO}_2)_2]_2$, which is one of the most stable MOFs) as the core. MIL-101 was used as the template and also as the C and Cr source. The synthesis process of the $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ composite is illustrated in Scheme 1. First, MIL-101 octahedra were synthesized using terephthalic acid (BDC) and Cr^{3+} as the organic ligand and central metal ion, respectively, under hydrothermal conditions. Then, the prepared MIL-101 particles were used as the core to form MIL-101@ TiO_2 (MT) core-shell structures via the hydrothermal method using TiF_4 as the titanium precursor. Lastly, the prepared core-shell MT particles were carbonized under N_2 atmosphere at 500°C for 5 h, and the core-shell $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ particles were obtained.

Scheme 1. Schematic illustration of synthesis of $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$.

2. Experimental

2.1. Chemicals and materials

All chemicals and reagents were of analytical grade. $\text{Cr}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$, BDC, titanium tetrafluoride, and hydrofluoric acid (HF) were purchased from Baierdi Chemical Reagent Co. Ltd. (Hefei, China); *N,N*-dimethylformamide (DMF) and ethanol were purchased from Langquan Chemical Reagent Co. Ltd. (Wuhu, China); and deionized water was obtained using a water purification system.

2.2. Synthesis of MIL-101

First, 0.8 g $\text{Cr}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$ and 0.3 g BDC were dissolved in 14 mL deionized water. The solution was stirred for 15 min, then 0.1 mL HF (40 wt%) was added to it, and stirring was continued for another 10 min. The mixed solution was loaded into a 25 mL Teflon-lined steel autoclave and then it was heated at 180°C for 20 h. After cooling, the sample was collected via centrifugation and washed with DMF and ethanol four times. Lastly, the obtained product was dried in an oven at 60°C before further use.

2.3. Synthesis of MT

First, 52 mg MIL-101 powder was dispersed in 10 mL ethanol via stirring, and then 3 mL 0.022 M TiF_4 aqueous solution was added to the dispersion. After stirring for another 5 min, the mixture was loaded into a 25 mL Teflon-lined steel autoclave at 180°C for 14 h. Lastly, the obtained sample was washed with deionized water and ethanol four times and was dried in an oven at 60°C before further use.

2.4. Synthesis of $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ core-shell structures

First, 0.1 g MT powder was added to four quartz crucibles of the same specifications. Then, N_2 protective calcination was successively carried out at 400, 500, 600, and 700°C and the samples obtained were denoted MT400, MT500, MT600, and MT700, respectively. The heating and cooling rates were controlled to be $2^\circ\text{C}/\text{min}$ and the holding time was 5 h.

3. Results and discussion

The crystal structure of MT was characterized using X-ray diffraction (XRD). The characteristic peaks in the XRD profile of

Fig. 1. Scanning electron micrographs of (a) MIL-101(Cr) and (b and c) MIL-101@TiO₂. (d) Transmission electron micrograph of MIL-101@TiO₂.

MT indicated the coexistence of anatase TiO₂ and MIL-101 in its structure (Fig. S1). The thermal gravimetric analysis (TGA) of MIL-101 in air revealed that it lost 75% of its total mass in two steps when the temperature was increased to 700 °C (Fig. S2(a)). The initial 10% weight loss below 200 °C corresponded to the volatilization of the surface-adsorbed solvent molecules [45], and the weight loss in the temperature range of 300–400 °C could be attributed to the pyrolysis of MIL-101. The TGA of MT only revealed the total mass of 20% when the temperature was increased to 700 °C (Fig. S2(b)). Therefore, using the weight loss data, we hypothesized that the as-synthesized MT sample contained approximately 27 wt% MIL-101 and 73 wt% TiO₂. The morphology of the synthesized MT was studied using scanning electron microscopy (SEM). The MIL-101 particles were octahedral and their diameter ranged from 300 to 500 nm (Fig. 1(a)). Many TiO₂ particles were uniformly dispersed on the surface of MIL-101 to form the core-shell structure (Fig. 1(b) and (c)). To further elucidate the structure of MT, we used transmission electron microscopy (TEM). The bright and dark areas in the TEM image of MT confirmed the core-shell nature of MT (Fig. 1(d)). Even though MIL-101 shrunk considerably

during the hydrothermal reaction, the TiO₂ shell was still stable, and therefore it maintained its basic octahedral shape.

The characteristic absorption bands of the oxygen-containing functional groups were observed in the Fourier-transform infrared spectroscopy (FT-IR) profile of MIL-101 (Fig. 2(a)), and the absorption peaks at 1400 and 1610, 1524, and 1700 cm⁻¹ represent the asymmetric stretching of the C–O–C carboxylate group in the BDC ligand, typical vibration of the stretching of the C=C bonds of the benzene ring, and symmetric stretching of the C=O carboxylate group in the BDC ligand, respectively [46]. The FT-IR spectrum of the MT composite was similar to that of MIL-101, which indicated that MIL-101 was still present in the structure of MT after the hydrothermal reaction. After calcination, almost all functional groups peaks disappeared and the C in MIL-101 formed Cr₂O₃/C@TiO₂ under the protection of N₂. The TGA curves of the samples also indicate that when the temperature exceeded 400 °C MIL-101 was sufficiently pyrolyzed (Fig. S2), and was transformed into CO₂ and Cr₂O₃ during calcination. The peaks at 148.3, 396.0, 513.8 and 634.6 cm⁻¹ in the low frequency region of the Raman spectrum of Cr₂O₃/C@TiO₂ (Fig. 2(b)) were assigned to anatase TiO₂, and the peaks at ~1359 and ~1607 cm⁻¹ corresponded to the D- and G-bands of C, respectively [47]; moreover, the presence of the G-band indicated the presence of *sp*² hybridized C in the samples [48]. Therefore, the Raman spectra confirmed the presence of C in the Cr₂O₃/C@TiO₂ composite. C could increase the electrical conductivity of TiO₂ and facilitate its electron transfer, which is beneficial for its photocatalytic efficiency.

MT was calcined at 400, 500, 600, and 700 °C for 5 h under N₂ atmosphere in a tube furnace. According to the SEM images (Figs. S3(a)–(d)), the morphologies of MT400 and MT500 were almost identical, and the samples maintained their core-shell structure, whereas the MT600 and MT700 samples collapsed and broke into debris. The XRD patterns of the MT samples are presented in Fig. 3. The characteristic peaks of MIL-101 disappeared after calcination, and all the diffraction peaks of MT400 could be readily indexed to anatase TiO₂ (JCPDS No. 21-1272). The diffraction peaks in the 2θ range of 24.5°–26.0° slightly shifted toward higher 2θ values as the calcination temperature increased (Fig. 3(b)), which indicated that some Ti⁴⁺ ions in the lattice sites of TiO₂ had been replaced by Cr³⁺. Two new diffrac-

Fig. 2. (a) Fourier-transform infrared spectra of MIL-101(Cr), MT (MIL-101@TiO₂) and MT500 (Cr₂O₃/C@TiO₂) and (b) Raman spectra of MT500.

Fig. 3. (a) X-ray diffraction patterns of prepared samples: diffraction peak positions of (b) (101) plane of TiO_2 in the 2θ range of 24.5°–26° and (c) Cr_2O_3 in the 2θ range of 33°–37°.

tion peaks at $2\theta = 33.7^\circ$ and 36.4° were observed in the XRD profile of MT500, which could be indexed to the (104) and (110) lattice planes of rhombohedral Cr_2O_3 (JCPDs No. 38-1479) (Figs. 3(a) and (c)), respectively. The intensity and sharpness of the TiO_2 and Cr_2O_3 peaks in the XRD profiles of MT600 and MT700 were slightly higher than those in the profiles of MT400 and MT500, which indicated that the crystallinity of the MT600 and MT700 samples was higher than that of the MT400 and MT500 samples.

After calcination, the overall octahedral morphology of MT500 was well preserved, the diameters of the octahedra ranged from 500 to 1000 nm, and the surface of the octahedra become rougher (Fig. 4(a)). The highly magnified SEM image of one octahedron in Fig. 4(b) reveals the presence of many nanoparticles on the surface of MT500. The core-shell structure

of the $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ octahedra could be observed in their TEM images (Figs. 4(c) and (d)). The high-resolution TEM image of the TiO_2 shell (inset of Fig. 4(c)) revealed that the interplanar d-spacing of the lattice fringes was 0.35 nm, which corresponded to the (101) lattice plane of anatase TiO_2 . Moreover, the inner cavities in the structure of MT500 are revealed by the sharp contrast between the hollow interior and outer shell (Fig. 4(d)). The porosity of MT500 was investigated using N_2 adsorption-desorption isotherms, and the Brunauer-Emmett-Teller (BET) specific surface areas of MIL-101, MT, and MT500 were determined to be approximately 2389, 454, and $65 \text{ m}^2 \text{ g}^{-1}$, respectively (Fig. S4). The BET specific surface area of these samples decreased sharply owing to the decomposition of MIL-101 during calcination. To further characterize the core-shell structure of MT500, energy-dispersive X-ray spectroscopy (EDS) mappings have been obtained. The EDS mappings in Figs. 4(e)–(h) illustrate that Cr, C, Ti, and O are not uniformly distributed throughout the entire octahedral architecture. C and Cr formed during the calcination of the MIL-101 precursor. Cr was mainly located in the core area, Ti was mainly distributed in the shell of MT500, and O was distributed homogeneously throughout the entire core-shell structure. These results demonstrated that Cr^{3+} in the core was converted to chromium oxides. In addition, a small amount of Cr was evenly distributed on the shell, and that was attributed to the Cr doping of the TiO_2 lattice. The obtained Cr-doped TiO_2 shell would narrow the bandgap of TiO_2 , and thus, it would enhance the visible light photocatalytic activity of $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$.

Figure 5 displays the optical properties of the as-synthesized samples, which were obtained using ultraviolet-visible (UV-vis) absorption spectroscopy. The absorbance edge of pristine TiO_2 was approximately 390 nm (Fig. 5(a)). The absorption edges of MT and MT500 were greatly red-shifted compared to that of TiO_2 . As the calcination temperature of MT increased, the absorption edge of the samples first shifted toward the red visible light region and then slightly toward the blue visible light region (Fig. S5(a)). The bandgaps of the samples could be estimated using the Kubelka-Munk function. The bandgaps of pristine TiO_2 and MT were estimated to be approximately 3.2 and 3.1 eV using the onsets of the curve edges, and these values indicated that the bandgap of TiO_2 became narrower after it was combined with MIL-101. MT500

Fig. 4. (a and b) Scanning and (c) transmission electron micrographs of MT500; inset of (c) high-resolution transmission electron micrograph of MT500. (d) Scanning transmission electron micrograph and (e, f, g, and h) Cr, Ti, O, and C energy-dispersive X-ray spectroscopy mappings, respectively, of MT500.

Fig. 5. (a) Ultraviolet-visible absorption spectra and corresponding Kubelka-Munk function vs. the photon energy of prepared samples (b).

presented two distinct absorption edges, which corresponded to TiO₂ and Cr₂O₃. The absorption edge of TiO₂ in the MT sample noticeably red shifted, which was attributed to the Cr³⁺ ions being doped into TiO₂ after the heat treatment and a new energy level being introduced into Cr-doped TiO₂ to reduce its bandgap [49]. The main bandgap of Cr-doped TiO₂ in MT500 was estimated to be approximately 2.39 eV, which indicated its good visible light absorption capacity. The visible light response of MT500 could be ascribed to the Cr-doping inducing the appearance of some additional energy levels, such as the Cr 2*p* level and O vacancies within the bandgap of TiO₂ [50]. Furthermore, the MT500, MT400, and MT700 samples displayed strong absorption over the entire visible light range, which could be attributed to the presence of C in these nano-

composites. As expected from the bandgap changes, the color of TiO₂, MT, and MT500 changed from white to yellow. These results suggested that the MT500 sample might be able to absorb more light and generate more electron-hole pairs, and thus could present better photocatalytic H₂ evolution activity than pure TiO₂.

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface composition and chemical valence states of various elements comprising MT500. The XPS survey profile confirmed the presence of Cr, O, Ti, and C in the structure of MT500 (Fig. 6(a)). The high-resolution Cr 2*p*, Ti 2*p*, and O 1*s* XPS profiles of MT500 are depicted in Figs. 6(b), (c), and (d), respectively. The two prominent peaks at 577.0 and 586.4 eV in Fig. 6(b) and S6(a) are assigned to Cr 2*p*_{3/2} and Cr 2*p*_{1/2} respec-

Fig. 6. X-ray photoelectron spectroscopy profiles of MT500: (a) survey, (b) Cr 2*p*, (c) Ti 2*p*, and (d) O 1*s*.

tively, and indicate the normal state of Cr^{3+} in the prepared samples. The binding energies of approximately 458.4 and 464.2 eV corresponded to $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$, respectively (Fig. 6(c)). The $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ peaks of pristine TiO_2 were located at approximately 458.7 and 464.4 eV (Fig. S7(a)). The binding energies of $\text{Ti } 2p$ (458.4 and 464.2 eV) for the MT500 sample were lower than those of the prepared pristine TiO_2 , and that could be attributed to the substitution of Ti^{4+} by Cr^{3+} . As the calcination temperature increased, the peak values shifted toward smaller angles (Fig. S6(b)), which should be attributed to more Ti^{4+} in the TiO_2 lattice being replaced by Cr^{3+} . Figure 6(d) displays the $\text{O } 1s$ XPS profile of MT500. That could be deconvoluted into two peaks at 529.9 and 531.5 eV, which were attributed to the lattice O in the TiO_2 phase [34] and surface-adsorbed O, respectively. The $\text{O } 1s$ XPS profile of pristine TiO_2 is very similar to that of MT500 (Fig. S7(b)). The high peak of MIL-101 (Fig. S6(c)) at ~ 531.5 eV could be attributed to the functional groups present on its surface, and this peak faded away when MIL-101 was calcined. The $\text{C } 1s$ XPS profile of the prepared samples is illustrated in Fig. S6(d). The main peak observed at 284.8 eV corresponded to the C–C species, and the other weak peak at 288.7 eV was assigned to the C=O groups of BDC in MIL-101.

The photocatalytic activity of the prepared samples was evaluated for the photocatalytic production of H_2 from water in the presence of methanol as the sacrificial agent under the irradiation of a 300 W Xe arc lamp. When the reaction mixture was kept under dark or in the absence of photocatalysts, no H_2

was formed, which indicated that both light and the photocatalysts were required to generate H_2 . The photocatalytic H_2 production under the irradiation of the full-spectrum 300 W Xe arc lamp is presented in Figs. 7 (a) and (b). The bar graph in Fig. 7(a) suggests that MIL-101 exhibited no activity for the H_2 production reaction, which indicated that MIL-101 was not an effective photocatalyst by itself. The photocatalytic activity of the pristine TiO_2 particles was low and the H_2 evolution rate was $114 \mu\text{mol h}^{-1} \text{g}^{-1}$, which was attributed to the fast recombination of the photogenerated charge carriers and limited utilization of the visible light spectrum [51]. The H_2 evolution rate over the MT nanocomposites was greatly decreased, which was ascribed to the combination of MIL-101 and TiO_2 . The H_2 evolution rate over MT400 was significantly higher than that of pristine TiO_2 , and the H_2 yield rate over MT400 was $300 \mu\text{mol h}^{-1} \text{g}^{-1}$, which was approximately 2.6 times higher than that over pure TiO_2 . The photocatalytic water splitting performance over MT500 was further improved. The optimized H_2 evolution rate of MT500 was $446 \mu\text{mol h}^{-1} \text{g}^{-1}$, which was approximately 3.9 times higher than that of pristine TiO_2 . The apparent quantum yield (AQY) of the H_2 evolution reaction of the MT500 photocatalysts at $\lambda = 365 \pm 5$ nm was measured to be 1.2%, which was approximately 3 times higher than that of pristine TiO_2 (AQY = 0.31%). However, the AQY value of MT500 was lower than the previously reported ones [24–27], and could be further increased by using co-catalysts. The photocatalytic activity of the MT600 and MT700 samples was lower than that of the MT500 sample. To study the factors that affected the pho-

Fig. 7. (a) Rate of H_2 production and (b) time evolution of photocatalytic H_2 production over synthesized photocatalyst samples under the irradiation of a 300 W Xe arc lamp. (c) Cyclic H_2 production over MT500 photocatalyst. (d) Time evolution of H_2 production over prepared photocatalyst samples under visible light ($\lambda > 420$ nm) irradiation.

photocatalytic activity of the MT samples in this study, MT was calcined at 500 °C in air, and the obtained specimen was denoted MT air. The H₂ evolution rate of MT air was 196 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which was only half of that of MT500. These results indicated that the presence of C, which derived from MIL-101, in the structure of MT500 was beneficial for enhancing the photocatalytic activity of MT500. The incorporated C could improve the electron transfer and promoted the separation of the photogenerated electron-hole pairs, as reported in several recent papers [52–54]. The stability of MT500 was evaluated over four consecutive photocatalytic cycles that were performed under the same conditions (Fig. 7(c)). We determined that 94.8% of the H₂ evolution rate was retained after three runs, which indicated the good stability of Cr₂O₃/C@TiO₂ for the photocatalytic H₂ evolution reaction. No noticeable changes in structure were observed for the MT500 photocatalyst after three runs (12 h) during the performance test, and that was confirmed using XRD and SEM analyses (Figs. S8 and S9, respectively). The UV-vis spectra of the prepared Cr₂O₃/C@TiO₂ catalyst revealed that it presented strong visible light absorption. Therefore, the photocatalytic H₂ production over the as-prepared samples was also evaluated under visible light irradiation ($\lambda > 420 \text{ nm}$) using methanol as the sacrificial agent, and the results are illustrated in Fig. 7(d). For comparison, Cr₂O₃/C was obtained via the calcination of pristine MIL-101 at 500 °C under N₂ flow. The XRD pattern and SEM image of Cr₂O₃/C are presented in Fig. S10. The photocatalytic activity of Cr₂O₃/C was very low, and its H₂ evolution rate was approximately 2 $\mu\text{mol h}^{-1} \text{g}^{-1}$. The H₂ evolution rates of the MT500 and MT700 samples were 25.5 and 13.3 $\mu\text{mol h}^{-1} \text{g}^{-1}$, respectively. The high calcination temperature of MT700 led to the its photocatalytic activity being lower than that of MT500. This decrease was probably due to the collapsing of the core-shell nanostructure and growth of grains at high temperature, as illustrated in Fig. S3(d).

To investigate the migration and separation of the photoinduced electron-hole carriers, MT500, MT, and TiO₂ samples were subjected to photoelectrochemical measurements. The photocurrent-time curves of the above-mentioned samples during typical on-off cycles under the applied potential of 0.4 V (vs. Ag/AgCl) are depicted in Fig. 8(a). The photocurrent density of the MT500 sample was significantly higher than those of the other two samples, which was consistent with the superior

photocatalytic performance of MT500 compared to those of MT and TiO₂. The photocurrent density of MT500 was approximately 2.1 mA cm⁻², which was ~3.5 and 5.5 times higher than those of pristine TiO₂ and MT, respectively. These results strongly indicated that the separation of the photogenerated electron-hole pairs of MT500 was promoted. Additionally, the electrochemical impedance spectra (EIS) Nyquist plots were used to investigate the charge transfer resistance of the above-mentioned samples, and the results are presented in Fig. 8(b). The Nyquist semicircle of MT500 was smaller than those of MT and TiO₂, which indicated that the charge transfer resistance of MT500 was lower than those of the other two samples. The photoluminescence (PL) spectra of pristine TiO₂, MT, and MT500 are presented in Fig. 8(c) and provided additional evidence for the improved charge carrier transport of MT500. The PL intensity of MT was slightly lower than that of pristine TiO₂, and the PL intensity of MT500 was much weaker than that of MT, which suggested that the lifetime of the photogenerated charge carriers of MT500 was longer than that of MT.

The photocatalytic activity of MT500 toward the photocatalytic H₂ production reaction was higher than those of the other samples mainly owing to following three reasons. (1) The bandgap of the TiO₂ shell, which was narrowed owing to Cr³⁺ doping, conferred the synthesized Cr₂O₃/C@TiO₂ a wide visible light photoresponse range. Consequently, Cr₂O₃/C@TiO₂ was able to harvest more visible light, and therefore, the photocatalytic performance of MT500 was improved. (2) Cr₂O₃/C, which was derived from MIL-101, enhanced the visible light absorption and formed a Z-scheme system with TiO₂, which was beneficial for improving its photocatalytic activity. C acted as the solid state electron mediator in Cr₂O₃/C@TiO₂. (3) The combination of Cr₂O₃, C, and TiO₂ into micro-octahedra could present synergistic effect for the H₂ evolution reaction, and could provide more active sites for the reaction.

The Mott-Schottky plots of the samples were obtained to investigate the band structure of TiO₂ and Cr₂O₃, as illustrated in Fig. S11. The extrapolated flat-band potentials of TiO₂ and Cr₂O₃ were determined to be -0.78 and -0.45 V (vs. Ag/AgCl, pH 7), respectively. The flat-band potentials of TiO₂ and Cr₂O₃ could be calculated as follows [27]:

$$E(\text{RHE}) = E(\text{Ag/AgCl}) + E^0 + 0.059 \text{ pH} \quad (1)$$

$$E^0(\text{Ag/AgCl}) = 0.197 \text{ V} \quad (2)$$

The flat-band potentials of TiO₂ and Cr₂O₃/C were -0.18 and

Fig. 8. (a) Photocurrent density at 0.4 V vs. Ag/AgCl under 300 W Xe arc lamp irradiation. (b) Electrochemical impedance spectra Nyquist plots and (c) photoluminescence spectra of pristine TiO₂, MT, and MT500.

Fig. 9. Proposed mechanism for photocatalytic H_2 production via water splitting over $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ composite. Here NHE denotes the normal hydrogen electrode.

0.16 V (vs. RHE, pH 0), respectively. The bandgap of pristine TiO_2 was calculated to be ~ 3.2 eV using its UV-vis absorption spectrum (Fig. 5). Pure Cr_2O_3 was obtained via the calcination of pristine MIL-101 at 500 °C in air. The UV-vis absorption spectra of Cr_2O_3 is presented in Fig. S12, where the bandgap of pure Cr_2O_3 is approximately 2.7 eV. The top of the valence band (VB) of Cr-doped TiO_2 was elevated by the occupied Cr^{3+} level; however, the original bottom of the conduction band (CB), which was determined by the Ti 3d orbital was hardly affected [55]. Therefore, the flat-band potential of Cr-doped TiO_2 was still -0.18 V. Using these results, the schematic illustration of the possible mechanism of the enhanced photocatalytic activity of $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ as a Z-scheme system is depicted in Fig. 9. Under irradiation, both Cr-doped TiO_2 and Cr_2O_3 could become photoexcited and produce photogenerated carriers. The photogenerated electrons in the CB of Cr_2O_3 would be transferred to C, then to the VB of TiO_2 , and then they would recombine with the holes photogenerated in TiO_2 . The photoexcited electrons in the CB of TiO_2 and holes in the VB of Cr_2O_3 would present strong reduction and oxidation capacities, respectively; they would transfer to the surface to react with water and would result in the high photocatalytic activity of $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ toward the photocatalytic H_2 evolution reaction.

4. Conclusions

$\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ composites were fabricated via the calcination of core-shell MT. MIL-101, which presented high surface area, was used as the template, Cr, and C source, and that led to the formation of the Cr-doped TiO_2 shell and $\text{Cr}_2\text{O}_3/\text{C}$ core. The visible light response range of the synthesized $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ was wide, which was beneficial for harvesting visible light and improving its photocatalytic performance for the H_2 production reaction. The photocatalytic activity of MT500 was excellent and its maximum H_2 evolution rate was $446 \mu\text{mol h}^{-1} \text{g}^{-1}$, which was approximately four times higher than that of pristine TiO_2 nanoparticles. The H_2 evolution rate over MT500 under visible light irradiation ($\lambda > 420$ nm) was $25.5 \mu\text{mol h}^{-1} \text{g}^{-1}$. The photocatalytic performance of MT500 was superior to that of TiO_2 , and that was mainly attributed to its wide visible light response range and efficient separation of photogenerated electron-hole pairs. This paper provides useful information for designing and preparing highly efficient photocatalytic systems.

Supporting information

Characterization method, photoelectrochemical measurements, photocatalytic hydrogen production, XRD, TG-DTA, SEM, BET, UV-vis, XPS.

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Graphical Abstract

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Synthesis of core-shell nanostructured $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ for photocatalytic hydrogen production

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$\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ nanocomposites were fabricated via the calcination of core-shell MIL-101@ TiO_2 , where MIL-101, which presented high surface area, was used as the template, Cr, and C source. The photocatalytic performance of the obtained $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ nanocomposites for the H_2 production reaction was significantly higher than that of pristine TiO_2 .

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 $\text{Cr}_2\text{O}_3/\text{C}@\text{TiO}_2$ 核壳型复合材料的设计合成及其光催化产氢性能

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摘要: 随着社会经济的快速发展, 能源危机和环境污染问题成为世界各国关注的焦点。通过光催化剂将太阳能用于污染物降解、分解水产氢、 CO_2 还原及有机物合成等领域, 是解决上述问题的理想途径。过渡金属氧化物 TiO_2 因其稳定性高、催化活性好、制备简单等优点, 被认为是最理想的光催化材料。然而, TiO_2 带隙较宽、光响应范围窄、光量子效率低等缺点限制了其实际应用。将碳或 Cr_2O_3 与 TiO_2 结合形成复合结构已被证明可以有效提升其光催化性能。另一方面, 金属离子的掺

杂可以有效提高氧化钛的可见光响应。

本文利用具有高比表面积金属有机骨架材料MIL-101(Cr)纳米材料作为模板、镉源和碳源,首先在MIL-101(Cr)表面可控生长 TiO_2 纳米颗粒,获得MIL-101(Cr)@ TiO_2 复合结构;然后在氮气保护下碳化形成 $\text{Cr}_2\text{O}_3/\text{C}@ \text{TiO}_2$ 核壳型复合材料。碳化后,制备的复合材料具有模板的八面体形貌和高比表面积, MIL-101(Cr)中的Cr元素一部分会形成 Cr_2O_3 ,一部分会掺杂到 TiO_2 中,使得 TiO_2 的吸收边红移。此外, $\text{Cr}_2\text{O}_3/\text{C}@ \text{TiO}_2$ 中的C有利于光的吸收和载流子的分离。这种独特的纳米结构赋予 $\text{Cr}_2\text{O}_3/\text{C}@ \text{TiO}_2$ 复合材料优异的光催化性能。在300 W氙灯照射下,该复合材料光解水产氢的速率为 $446 \mu\text{mol h}^{-1} \text{g}^{-1}$,约为纯 TiO_2 的4倍。在可见光照射下, $\text{Cr}_2\text{O}_3/\text{C}@ \text{TiO}_2$ 分解水产氢的速率为 $25.5 \mu\text{mol h}^{-1} \text{g}^{-1}$ 。将获得的粉体催化剂制备成光电极发现, $\text{Cr}_2\text{O}_3/\text{C}@ \text{TiO}_2$ 在全幅光照射下的光电流密度在0.4 V (vs.Ag/AgCl)下达到 2.3 mA/cm^2 ,约为纯 TiO_2 的3.5倍。 $\text{Cr}_2\text{O}_3/\text{C}@ \text{TiO}_2$ 光催化产氢活性的提高一方面是由于Cr掺杂到 TiO_2 中使得其具有可见光响应,另一方面MIL-101碳化获得的 $\text{Cr}_2\text{O}_3/\text{C}$ 有效促进了光生载流子的分离。

关键词: 核壳结构; Cr_2O_3 ; 二氧化钛; 产氢; 光催化剂

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