Highly Performance Core-Shell TiO$_2$(B)/anatase Homojunction Nanobelts with Active Cobalt phosphide Cocatalyst for Hydrogen Production

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In this paper, a highly efficient core-shell structure of TiO$_2$(B)/anatase photocatalyst with CoP cocatalyst has been synthesized via hydrothermal processes and a mechanical milling method. The designed core-shell TiO$_2$(B)/anatase photocatalysts exhibit excellent performance by compared with pure TiO$_2$(B) and anatase phase. With the participation of CoP particles, there is drastically enhanced photocatalytic activity of TiO$_2$(B)/anatase, and the H$_2$-production rate can be up to 7400 μmol·g$^{-1}$, which is about 3.2 times higher than TiO$_2$(B)/anatase photocatalyst. The improved activity is attributed to the contribution of the well-matched core-shell structure and cooperative effect of CoP cocatalyst. The photogenerated holes of anatase can migrate more promptly to the adjacent TiO$_2$(B) core than the photogenerated electrons, which result in an accumulation of electrons in the anatase, and CoP nanoparticles can contribute significantly to transferring electrons from the surface of TiO$_2$(A). It was found that the efficient separation of electron-hole pairs greatly improved the photocatalytic hydrogen evolution in water under UV light irradiation.

Photocatalytic hydrogen production from water using solar energy has received increasing attention because this strategy is considered to be a globally accepted way for solving the energy problem. Titanium dioxide (TiO$_2$), especially anatase phase photocatalysts, has attracted significant attention in photocatalytic hydrogen evolution due to its low cost, excellent chemical stability and superior photocatalytic activity. Nevertheless, TiO$_2$ can only be motivated by UV-light due to its large band gap (3.2 eV), and the fast recombination of photogenerated electrons and holes limits the application of TiO$_2$. Therefore, many researchers focus on TiO$_2$ to make it sensitive to visible light and to inhibit the recombination of photogenerated charge carrier, which affect its overall photocatalytic efficiency.

Construction of homojunction photocatalysts might be a common and effective way to improve the separation efficiency of photoinduced electron-hole pairs. The commercially available photocatalysts, such as Degussa P25 TiO$_2$, has been found to exhibit a better photoactivity than pure anatase in many reaction systems. The efficient electron and holes transferring between the two phases can increase lifetime of electrons and holes. Coincidentally, a relatively new TiO$_2$(B) crystal phase is observed, which shows different crystal structures with anatase, rutile, and brookite. Although the photocatalytic efficiency of TiO$_2$(B) is lower than anatase, the former phase possesses a narrow bandgap and specific conduction band (CB) and valence band (VB) edge potential. Thus, the potential difference between the CB and VB edges of the two phases can promote charge transfer from one phase to the other when TiO$_2$(B) and anatase combined with each other forming a homojunction. Li et al. synthesized core-shell anatase/TiO$_2$(B) nanofiber, which shows enhanced photocatalytic activity compared to either single-crystal anatase or single-crystal TiO$_2$(B) nanofiber. Li's group synthesized TiO$_2$(B)-anatase...
homojunction with disordered surface shell, and the excellent performance for photocatalytic hydrogen evolution was 580 μmol h⁻¹ under simulated solar light irradiation (0.02 g photocatalyst)⁴⁶.

Although homojunction can improve the charge transfer, the H₂-production efficiency of TiO₂(B)/anatase is still limited because the accumulated electrons in CB may recombine with the holes in VB easily. So, it is a wide and effective strategy to load proper oxidation or reduction cocatalysts on the surface of semiconductor photocatalysts¹⁷⁻¹⁹. Various kinds of cocatalysts have been applied to TiO₂ photocatalysts to improve the activity of H₂ evolution reactions, including metal cocatalysts, metal oxide/sulfide cocatalysts and noble metals (e.g. Pt, Ag, Au and Ru)²⁰⁻²⁵. However, the preparation of these cocatalysts particles is complicated and quite expensive for widespread practical application. A variety of non-precious cocatalysts have been reported, including MoS²⁶, Cu(OH)²⁷, NiS²⁸, NiO²⁹. Recently, transition metal phosphides, including Ni₃P, CoP, FeP, MoP and Cu₃P have been exploited in electrocatalysis of the hydrogen evolution reaction, and achieved outstanding efficiency³⁰⁻³². During these pioneering works, it has been noticed that CoP nanoparticles show good electrical conductivity with metallic behavior. Chen's group discovered that CoP nanoparticles together with CdS nanorods exhibited excellent efficiency for photocatalytic hydrogen evolution³³,³⁴. We envision that the hydrogen production performance can be dramatically improved by choosing CoP cocatalysts nanoparticles.

Herein, we designed TiO₂(B)/anatase core-shell homojunction nanobelts using CoP nanoparticles as cocatalysts for efficient photocatalytic H₂ production from aqueous methanol solution. The electrons migrate to the same destinations are times longer than holes in TiO₂(B)/anatase system, and the accumulated electrons can be easily separate and transfer with the participation of CoP cocatalyst. The subsequently photocatalytic H₂-production reduction reactions can be effectively enhanced. So, it is believed that this strategy is feasible and will have great practical application for hydrogen production.

Experimental

Synthesis of core-shell structure photocatalyst. Core-Shell TiO₂ nanobelts were obtained using a previously reported procedure³⁵. 3 g of anatase powder was mixed with 40 mL of 10 M NaOH solution. The suspension were dispersed in an ultrasonic bath for 30 min then transferred into into a Teflon-lined stainless steel autoclave, sealed and maintained at the temperature of 180 °C for 48 h. The precipitate (sodium titanate nanobelts) was collected, washed with distilled water several times to remove excess NaOH. Then, the obtained precursor was exchanged with H⁺ using a 0.1 M HCl solution for 24 h to form H₂TiO₇ nanofibers. The product washed again with distilled water to neutral and dried at 70 °C for 10 h. The core-shell photocatalyst was synthesized by hydrothermal treatment of precursors in an acid environment and further subjected to heating process. 0.8 g of H₂TiO₇ nanofibers were dispersed in a dilute (0.05 M, 80 mL) HNO₃ acid solution and kept at 110 °C for 48 h. The dried powder was heated in a muffle oven at 450 °C (2 °C/min) in air for 4 h, named T (A). Reference samples: (1) Anatase catalyst was prepared by prolonging the hydrothermal reaction (HNO₃ acid solution) time to 60 h and calcining at 450 °C in air for 4 h, noted as T (A); (2) TiO₂(B) catalyst was obtained by using dried H₂TiO₇ powder heated at 450 °C for 4 h, noted as T (B).

Synthesis of CoP nanoparticles. CoP nanoparticles were prepared via a thermal phosphidation reaction using Co(OH)₂, as precursor³⁶. 200 mg of Co(NO₃)₂·6H₂O was added to 100 mL aqueous solution containing 50 mg sodium citrate and stirred for 15 min. Then excess NaOH solution (0.5 M) was added to the mixture dropwise. The formed Co(OH)₂ suspension was separated by centrifugation and dried at vacuum oven. Afterwards, 50 mg of obtained Co(OH)₂ and 250 mg NaH₂PO₂ solid were ground in a mortar and put in a quartz boat. Subsequently, the samples were maintained in tube furnace at 300 °C for 1 h with a heating rate of 2 °C·min⁻¹ in a flowing Ar atmosphere (30 mL/min). Following cooling to room temperature, the obtained black solid was washed subsequently by water and ethanol three times and dried at vacuum oven.

Loading of CoP Cocatalyst. The loading of CoP nanoparticles on TiO₂(B)/anatase core-shell photocatalyst was conducted by a mechanical milling method, the preparation process as shown in Fig. 1.

Characterizations. X-ray diffraction (XRD) data of the as-synthesized samples were recorded by a Bruker D8A A252 X-ray diffractometer system using Cu Kα (λ = 0.15406 nm) radiation. The morphologies of the prepared samples were performed using a Hitachi SU-8010 instrument. High-resolution transmission electron microscopy (HR-TEM) and energy-dispersive X-ray spectroscopy (EDS) were applied to investigate the microstructure using a Tecnai G² F30 instrument (HR-TEM operated at 200 kV). The UV-vis diffuse reflectance (DR) spectra of the samples were tested on a Hitachi U-3010 double beam spectrophotometer. The photoluminescence (PL) spectra were measured on a high-resolution multi-function imaging spectrometer (iHR 550) using laser transmitter (532 nm). X-ray photoelectron spectroscopy (XPS) was performed on an K-Alpha spectrometer (THERMO FISHERSCIENTIFIC).

Photocatalytic H₂-production. The photocatalytic H₂-production experiment was carried out as follows, 100 mg photocatalyst and 10 mL methanol were added into the tube. Then the total volume of the mixed solution was adjusted to 100 mL with distilled water. A 300 W Xe lamp was used as light source and the electric current recorded to be 15 A. Before light irradiation, the gas-tight system was heated for several hours to make sure the tightness of all system and adsorption–desorption equilibrium between the photocatalyst and gases. The gas products were periodically analyzed by using a gas chromatography (GC-2014, Shimadzu Corp, Japan), which was equipped with a 5 Å molecular sieve column (3 m × 2 mm).

Results and Discussion

Figure 2 shows the XRD patterns of the as-prepared TiO₂(A), TiO₂(AB) and TiO₂(B) nanobelts. The obtained TiO₂(A) and TiO₂(B) samples are matched well with the crystal structure data of anatase phase (JCPDS No. 21–1272) and TiO₂(B) phase (JCPDS No. 46–1238)³⁶,³⁷. The peak of TiO₂(B) in the core-shell structure is not
obvious may attribute to the overlapped main peak between TiO$_2$(B) and TiO$_2$(A), or the low contents of TiO$_2$(B) for detection. In addition, as depicted in Figure S1, the XRD diffraction peaks of CoP nanoparticles are indistinguishable for each sample from CoP(0.5%)/TiO$_2$ to CoP(5%)/TiO$_2$ due to the low loading amount and weak crystallization of CoP nanoparticle. Similar phenomenon has been observed for other photocatalysts.$^{33,38}$

The scanning electron microscopy (SEM) characterization can provide the direct evidence for the coexistence of CoP and TiO$_2$. It can be seen that CoP nanoparticles are polydisperse (Figure S2a) and TiO$_2$(AB) are nanobelts-like morphologies (Figure S2b). After coating with CoP nanoparticles, Co and P elements are distributed well on the surface of TiO$_2$(AB) nanobelts photocatalyst (Figure S2c,d). The CoP-TiO$_2$(AB) composites structure can be further confirmed in the EDS mappings analysis presented in Figure S2e. The results indicate that the Co, P, Ti and O elemental are uniformly distributed, and no other elements are detected. Furthermore, the corresponding energy dispersive X-ray spectroscopy (EDX) analysis confirms the existence of CoP and TiO$_2$. However, the content of the measured CoP is lower than theoretical values in the final composites because of only surface CoP atoms can be checked (see Supplementary Figure S3).

To investigate the existence of core-shell homojunction, more explicit structure evolution is shown in transmission electron microscopy (TEM). As described in Fig. 3a, the typical TiO$_2$(B)/anatase core-shell nanobelts can be observed clearly. The core of the nanobelts is corresponding to TiO$_2$(B) phase, while the shell conforms to anatase phase. The HRTEM confirms that the sample possesses a homojunction structure with well-matched lattice fringes of the (110) plane of TiO$_2$(B) and (101) plane of anatase (Fig. 3b). The TEM images of CoP(1%)-TiO$_2$(AB) sample as depicted in Fig. 3c clearly indicate CoP nanoparticles (the red circle) are deposited on the surface of TiO$_2$(AB) photocatalyst. The HRTEM image further shows that TiO$_2$(AB) and CoP nanoparticles are in close contact with each other (Fig. 3d). The lattice spacings of ca. 0.35 nm and 0.19 nm belong to the diffraction planes of TiO$_2$(A) and CoP nanoparticles, respectively.
The optical properties of the TiO$_2$(B) and TiO$_2$(A) are investigated by UV-Vis diffuse reflectance spectra (DRS) as given in Fig. 4a. The absorption edges of pure TiO$_2$(B) and TiO$_2$(A) are 406 nm and 388 nm, respectively. According to Tauc formula $\alpha h\nu = A(h\nu - E_g)^n$, the band gaps of TiO$_2$(B) and TiO$_2$(A) are estimated to be...
3.05 and 3.19 eV, respectively (Fig. 4b). With the increasing loading of CoP, a red-shift DRS of is observed in the CoP-TiO₂(AB) composite materials, which can be attributed to the absorption of CoP nanoparticles (Fig. 4c). However, there is no significant absorption edge change of the CoP-TiO₂(AB) samples, indicating that CoP is incorporated onto the surface of TiO₂(AB) rather than into the lattice [34]. Besides, the color of the composite photocatalyst becomes brown due to the absorption of CoP particles. The XPS spectrum results of TiO₂(B), TiO₂(AB), TiO₂(A) and CoP are presented in Figure S4. The high resolution XPS spectrum shows O1s, Ti2p, P2p and Co2p, respectively. The binding energy of as-fabricated TiO₂(B), TiO₂(AB) and TiO₂(A) is not changed for both Ti2p and O1s. In addition, the binding energy peaks of P 2p and Co (2p3/2) are in agreement with the reported ones [33]. Compared with TiO₂(AB) (35.4 m² g⁻¹) sample, the as-prepared CoP(1%)-TiO₂(AB) composite sample shows a small specific surface area of 30.53 m² g⁻¹ (Figure S5).

The photocatalytic performances of the as-prepared TiO₂(A), TiO₂(B) and TiO₂(AB) samples are monitored for hydrogen production evolution from pure water containing methanol as sacrificial reagents under simulated sunlight irradiation. As plotted in Fig. 5a, it clearly seen that the core-shell structure TiO₂(AB) catalysts express the highest yield of H₂ with loading of 1% CoP cocatalysts. In the absence of cocatalysts, a sharp decrease of H₂ production is observed for TiO₂(A), TiO₂(B) and TiO₂(AB) samples. The highest H₂-production rate of CoP(1%)-TiO₂(AB) can be up to 7400 μmol g⁻¹, which is about 3.2-times higher than that of TiO₂(AB) (2306 μmol g⁻¹) (Fig. 5b). The notably performance imply that CoP is an effective cocatalyst, which show impact on enhancing the photocatalytic activity positive. To check whether H₂ produced is from water or methanol, blank experiments without catalysts is conducted. There is no H₂ generation that suggested water is probably the real substrate in the photocatalytic reaction, and the conclusion is also verified by other authors [33,39]. The photocatalytic activity of the core-shell structure TiO₂(AB) photocatalysts with different mount of CoP cocatalysts are also studied (Fig. 5c). As the amount of CoP increases, the H₂ evolution rate is further enhanced, reaching the maximum value for CoP(1%)-TiO₂. However, there is a decrease in the photocatalytic H₂ evolution with further increase the loading amount of CoP particles. Hence, the optimal loading of CoP should be 1 wt%. The results may due to the following causes: (i) with the loading dosage of CoP cocatalysts, more active sites can be provided for reduction reactions; (ii) excessive CoP nanoparticles covered on the surface TiO₂(AB) or aggregated into larger nanoparticles shielding surface active sites, which may lead to a negative impact on their catalytic activity. This phenomenon is similar to other nanoparticle cocatalysts [33,42]. Figure 5d displays the durability of the photocatalysts after 50 hours irradiation, and the result indicate that a slight increase is measured with CoP cocatalyst. XRD patterns further demonstrate the stable of the as-prepared photocatalyst (Figure S6).

To further understand the enhancement of photocatalytic activity between Cop nanoparticles and TiO₂(AB) photocatalysts, transient photocurrent response and electrochemical impedance spectroscopy (EIS) are conducted under...
UV-visible light irradiation. Upon illumination, the photocurrent immediately rises and the photocurrent rapidly decreases to zero as long as the light is switched off. As presented in Fig. 6a, the pulsed photocurrent density of the CoP(1%)-TiO$_2$(AB) sample is higher than other photocatalysts, suggesting more efficient separation of photoexcited electron-hole pairs happened. In addition, CoP cocatalysts exhibit improved photocurrents (650 $\mu$A) compared with pure TiO$_2$(AB) (Fig. 6b). It is notable that the change tendency agrees well with the photocatalytic H$_2$ production activity. From the photoluminescence (PL) spectra in Fig. 6c, it can be seen that the emission intensity of the samples decreases in the following order: TiO$_2$(A) < TiO$_2$(B) < TiO$_2$(AB) < CoP(1%)-TiO$_2$(AB), indicating that charge recombination can be better suppressed after loading CoP cocatalysts. The PL emission bands at around 410 nm are observed in all samples, which belong to the emission of the band gap transition of TiO$_2$.

Figure 6. (a) Photogenerated currents density of the CoP(x%)-TiO$_2$ photocatalysts and (b) different TiO$_2$ phase under UV-visible light; (c) Photoluminescence (PL) spectra and (d) Nyquist impedance plots of TiO$_2$(A), TiO$_2$(B), TiO$_2$(AB) and CoP(1%)-TiO$_2$(AB) samples.

Figure 7. Mott-Schottky plot for (a) TiO$_2$(A) and (b) TiO$_2$(B) electrode in saturated Na$_2$SO$_4$ electrolyte solution (0.1 M, pH = 6.8) vs SCE.

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Furthermore, the impedance radius of CoP(1%)-TiO$_2$(AB) is smaller than TiO$_2$(AB) (Fig. 6d), indicating that CoP can enhance separation efficiency of the photogenerated charges and facilitate the interfacial charge transfer.
Mechanism of CoP-TiO$_2$(AB)

In order to investigate the transfer mechanism of electrons (e$^-$) and holes (h$^+$) between TiO$_2$(A) and TiO$_2$(B), the band edge positions of conduction band (CB) and valence band (VB) of the two semiconductor are measured by Mott-Schottky measurement, which can directly probe the energy positions of TiO$_2$(A) and TiO$_2$(B). From Fig. 7, the CB and VB edges of TiO$_2$(A) nanobelts are found to be $-0.19\,\text{eV}$ and $+3.05\,\text{eV}$ (vs. NHE), and the CB and VB edges of TiO$_2$(B) nanosheets are $-0.15\,\text{eV}$ and $+2.96\,\text{eV}$ (vs. NHE), respectively. The calculation will be essential for the verification as shown in Support Information (Table 1) and early reports$^{35,43,44}$. Accordingly, schematic diagram of the role of cocatalysts played in the separation and transfer of photogenerated charges of TiO$_2$(AB) core-shell homojunction is shown in Fig. 8. Based on the energy structure of the interface between TiO$_2$(A) and TiO$_2$(B), the photoinduced holes of TiO$_2$(A) could directly be injected into the VB of TiO$_2$(B). Meanwhile, the excited electrons in TiO$_2$(A) could be transferred to the CB of TiO$_2$(B) easily under the irradiation of UV light. In the transfer process, the early literature has verified that the photogenerated holes can migrate more promptly to the adjacent TiO$_2$(B) phase than the photogenerated electrons. Because the electrons migrate to the same destination in the same anatase crystals are 40 times longer ($>40–160\,\text{ps}$) than those for holes ($1–4\,\text{ps}$), which result in an accumulation of holes in the TiO$_2$(B)$^{35}$. These photoinduced holes at the VB of TiO$_2$(A) and TiO$_2$(B) can react with the H$_2$O to generate some oxidation groups such as hydroxyl radicals, causing the oxidation reaction with the sacrificial reagent employed such as CH$_3$OH. The overall outcome of the interphase charge migration is that a higher electron concentration left within the anatase shell. With the help of CoP cocatalyst, the photogenerated electrons on the CB of TiO$_2$(A) tend to transfer to the loaded CoP nanoparticles, which are capable of the reduction reaction. As a consequence, the loaded cocatalysts are very helpful to the separation and transfer of photogenerated electron-hole pairs. Hence, the coherent interface between anatase and TiO$_2$(B) structure and the CoP cocatalyst in the photocatalysis process may reduce recombination of photogenerated electron-hole pairs in the photocatalytic reaction and the photocatalytic activity is enhanced.

Conclusion

In summary, a highly efficient core-shell TiO$_2$(B)/anatase photocatalyst has been fabricated successfully for photocatalytic H$_2$ evolution. The designed homojunction photocatalysts exhibited excellent performance compared with the pure phase, and a drastically enhanced photocatalytic activity appears with the participation of CoP cocatalysts. The H$_2$-production rate of CoP(1%)-TiO$_2$(AB) photocatalysts can be up to 7400 $\mu\text{mol} \cdot \text{g}^{-1}$. The remarkable activity is attributed to the cooperative contribution of effective core/shell structure that leading to the separation of photogenerated charges and the function of CoP cocatalysts on the transfer of photogenerated electrons from anatase to outside driven by the cocatalysts. This work demonstrated the great feasibility of utilizing CoP cocatalyst of different core/shell system in the application of photocatalytic H$_2$- production.

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Acknowledgements
This work is supported by the National Natural Science Foundations of China (Grant No.21577132), the Fundamental Research Funds for the Central Universities (Grant No. 2652015225).
Author Contributions
G. Yang, H. Ding and D.M. Chen designed the main study. Jiejie Feng, Qiang Hao and Sijia Sun take part in the experiments. W.H. Ao analyzed the data. All authors reviewed the manuscript.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-017-15134-w.

Competing Interests: The authors declare that they have no competing interests.

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