Metal-Organic-Frameworks-driven hollow core-shell Co$_3$O$_4$/TiO$_2$ Heterojunction for Enhancement of Photocatalytic Hydrogen generation

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Abstract: In recent years, how to further enhance the efficiency of photocatalytic hydrogen generation has become a research hotspot. At present, the metal-organic-frameworks (MOF) has attracted much attention in the field of catalysis due to its special physical and chemical properties. Herein, the hollow core-shell Co$_3$O$_4$/TiO$_2$ heterojunction is prepared by deposition and annealing method with ZIF-67 as self-sacrificial templates and metal precurors. The characterization of XRD, SEM, and TEM indicate that the hollow core-shell Co$_3$O$_4$/TiO$_2$ heterojunction is synthesized successfully. The characterization of UV, PL indicate that the Co$_3$O$_4$/TiO$_2$ show superior photoelectric performance. By evaluation, the Co$_3$O$_4$/TiO$_2$ heterogeneous catalyst exhibits a remarkable photocatalytic hydrogen production performance, which is ~11 and ~14 times higher than that of pure Co$_3$O$_4$ and TiO$_2$. Studies prove that the formation of heterojunction can promote charge carriers separation, the hollow structure can raise the solar efficiency, offer more surface areas and active sites, all these are beneficial for photocatalytic performance.

1. Introduction
Recently, with the energy consuming crisis and environmental pollution issues, the development of renewable and pollution-free energy has attracted researchers’ attentions increasingly such as hydrogen fuel and solar energy et al.[1] Especially, the photocatalytic hydrogen generation(HER) is regarded as the most promising technology to convert solar fuel into chemical energy.[2] In past few decades, the TiO$_2$-based photocatalytic has been widely explored due to its suitable energy band structure, corrosion resistance and low cost.[3] However, the high recombination rate of photon-generated carriers and low active site area limit the application in photocatalytic water splitting.[4] Herein, the typical p-type semiconductor Co$_3$O$_4$, due to narrow band gap and abundant active sites, has been regarded as an ideal candidate material for construction of p-n heterostructures to improve the photocatalytic performance.[5]

It is worth mentioning that designing advanced structure is an efficient strategy to improve the photocatalytic activities.[6] In particular, the hollow structure has attracted great attention, because it can enhance solar light utilization, offer unique inner-external surface, and expose abundant active sites.[7] As reported, as one of the typical MOF, the zeolitic imidazolate framework(ZIF) exhibits novel properties, such diversity in structure, morphology and high specific surface area and thermal stability.[8] The above physical and chemical properties can be used as metal precurors and self-sacrificial templates.[9] For the Photocatalysis, the ZIF is an effective route to fabricate the hollow structure, avoiding the complicated process of removing templates.[10]
Herein, we have prepared hollow core-shell Co$_3$O$_4$@TiO$_2$ heterostructures nanocomposites via using ZIF-67 as self-sacrificial templates and metal precurors. Compared with pure TiO$_2$, the Co$_3$O$_4$@TiO$_2$ nanocomposites exhibits obvious enhancement in phoyocatalytic HER. In addition, mechanism of the heterojunction was also studied.

2. Experiment

2.1. Synthesis of ZIF-67
Firstly, the self-template and metal percusor of ZIF-67 was synthesised with some modification. Typically 0.6 g 2-methylimidazole was dissolved in 20 ml methanol solution. Subsequently, the 2-methylimidazole solution was dropped into 15 ml solution combined with 0.3 g Co(NO)$_3$·6H$_2$O and 20 ml methanol with 20 min stirring. Then the mixed solution was incubated at 25 °C for 3 hours. Finally, the prepared precipitate was washed by ethanol four times, dried in a hot vacuum drying oven at 70 °C overnight.

2.2 Synthesis of hollow core-shell Co$_3$O$_4$/TiO$_2$
Firstly, 0.5 ml titanium (IV) isopropoxide was dropped and mixed with 20 ml ethanol. 0.1 g ZIF-67 was put into 25 ml ethanol with sonicating for 5 min. Then, the above solutions were mixed with stirring for 6 h after dropping 0.5 ml distilled water. Subsequently, the obtained precipitate was centrifuged with ethanol, dried in a hot vacuum oven at 60 °C for overnight. Finally, the hollow core-shell Co$_3$O$_4$/TiO$_2$ nanocomposites were prepared by calcination at 450 °C (2°C/min) for 1 h in air.

2.3 Characterization
The phase and crystal structure of the samples were tested by X-ray powder diffraction. The morphology of the samples was characterized by FESEM (Hitachi S-4800) and TEM (JEM-2100). The UV and PL curves were characterized by spectrophotometer (Hitachi-U3900) and spectrophotomater (Hitachi F-7000). The HER characterization was obtained by Labsolar 6A photocatalytic system (Perfect Light Technology).

2.4 Photocatalytic activity
Photocatalytic HER performances were measured in a gas-sealed glass reactor and evacuation system. Typically, 25 mg catalyst was mixed with 80 ml Na$_2$S (0.25 M) and Na$_2$SO$_3$ (0.15 M) solution (sacrificial agent). A 300W Xe arc lamp was used as light source. Firstly, the air in reactor was remove by the high purity argon gas for 40 min. Then the solution was ultrasound for 15 min to obtain a uniform suspension. Finally, the suspension was put into the reactor for experiment. The actual production of H$_2$ was tested by Labsolar 6A photocatalytic system and gas chromatograph (Techcomp GC-7900).

3. Results and discussions

Fig.1. The XRD spectra of the samples
As shown in Fig. 1, the XRD results of TiO2, Co3O4, and Co3O4/TiO2. For the TiO2, diffraction peaks located at 25.28°, 38.22°, 48.23°, 54.18°, 55.28° and 63.01° are belong to the anatase phase TiO2(PDF#84-1285). What’s more, the new peaks at 31.30°, 36.91°, 38.58°, 44.81°, 59.45° and 65.33° can be ascribed to the Co3O4/TiO2 hollow core-shell heterojunction, which can be ascribed to the (202), (311), (222), (400), (511) and (440) planes of Co3O4 (PDF#74-2120). There is no extra peaks in all curves, that indicates the sample is composed of Co3O4 and TiO2.

Fig. 2. SEM and TEM of samples, (a) ZIF-67, (b,d) ZIF-67/Ti(OH)4, (c,e) Co3O4/TiO2; HRTEM of Co3O4/TiO2 (f).

The morphology of samples is exhibited in Fig. 2. As revealed in Fig. 2a, the as-prepared of ZIF-67 is a classical dodecahedral structure with a diameter of ~300 nm. Further, with the formation of ZIF-67/Ti(OH)4 sold-polyhedron (Fig.2b, d), the surface turns to be more coarse, and the diameter increases to about ~380 nm. Subsequently, after calcination, the sold-polyhedron is transformed into a complete hollow structure and Co3O4 nanoparticles are distributed on the inner surface of hollow shells of TiO2 (Fig.2c, e), which can provide efficient specific surface area and more active sites for HER. Finally, the high resolution TEM is shawn in images (Fig.2.f), the measured lattice length of 0.352 nm is assigned to the (101) plane of anatase TiO2 and the 0.244 nm is belonged to the (311) plane of Co3O4. These above results indicate that the hollow Co3O4/TiO2 heterojunction has been fabricated successfully.
Fig. 3. The UV-vis absorption spectra (a) and PL spectra (b) of as-prepared samples
As revealed in Fig. 3a, the pure TiO$_2$ exhibits the weakest light absorption and the absorption edge is located at ~380 nm. What’s more, the sample of Co$_3$O$_4$/TiO$_2$ exhibits significant absorption of visible light, because the band gap of Co$_3$O$_4$ is narrower than pure TiO$_2$. As revealed in Fig. 3b, the PL of the as-prepared Co$_3$O$_4$/TiO$_2$ is lower than both pure TiO$_2$ and Co$_3$O$_4$, which indicates that, due to the formation of pn junction, the separation and immigration of the photogenerated electron-hole pair become more effective. All above properties promote the performance of photocatalytic HER.

Fig. 4. The photocatalytic hydrogen production activity of as-prepared samples
The photocatalytic hydrogen generation capacity of the samples are shown in image 4. As revealed in Fig.4a, the Co$_3$O$_4$/TiO$_2$ heterostructure exhibits a remarkably superior HRE performance than both pure TiO$_2$ and Co$_3$O$_4$ during 4 hours reaction. By calculation, the rate of HER is revealed in Fig. 4b, herein, the hydrogen production rate of composited sample is 342.7 μmol (g·h)$^{-1}$, which is ~11 and ~14 times higher than that pure TiO$_2$ (30.5 μmol (g·h)$^{-1}$) and Co$_3$O$_4$ (25.3 μmol (g·h)$^{-1}$), respectively. These results indicate that the hollow core-shell Co$_3$O$_4$/TiO$_2$ heterostructures can increase the hydrogen generation performance efficiently.

4. Conclusion
In this work, the hollow core-shell Co$_3$O$_4$/TiO$_2$ heterogeneous been prepared by deposition-annealing method with ZIF-67 as self-sacrificial templates and metal precursors. By evaluation, the photocatalytic hydrogen production of Co$_3$O$_4$/TiO$_2$ exhibits obvious enhancing, that is ascribed to the formation of heterojunction can improve the efficiency of photogenerated electron-hole pairs separation, the hollow structure can raise the solar efficiency, offer more surface areas and active sites, all these are beneficial for photocatalytic performance. Consequently, this study provides an important basis to improve the photocatalytic performance by constructing heterojunction and regulating the morphology of the catalyst. Our research also extend the application of MOF in the field of photocatalysis.

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