TiO$_2$/Cyclodextrin Hybrid Structure with Efficient Photocatalytic Water Splitting

Siyao Guo, Jun Shang, Tiejun Zhao, Dongshuai Hou, Zuquan Jin, and Guoxing Sun

A novel TiO$_2$/β-cyclodextrin (TiO$_2$/β-CD) organic-inorganic hybrid nano-material with alveolate structure is fabricated using a facile one-step strategy. The alveolate TiO$_2$/β-CD hybrid nano-material exhibits outstanding photocatalytic activity and recyclability on photocatalytic water splitting. The production of H$_2$ evolution of TiO$_2$/β-CD hybrid reaches to 5800 μmolg$^{-1}$ after 8 h without noble metal. Meanwhile, the recyclability of the TiO$_2$/β-CD photocatalyst is found to be no obvious decrease with the H$_2$ generation after third successive runs. The formation of the oxygen defects occurred on coordinatively unsaturated Ti-sites by the introduction of β-CD at the outer surface of TiO$_2$ could be the predominant active species in the photocatalytic system. Due to the alveolate heterogeneous structure of TiO$_2$/β-CD hybrid play a role as “channel” for photocatalytic activity. The channel can capture more electrons and light, provides a larger area for reaction. This work provides a promising approach to construct noble metal-free and more stabilized organic-inorganic nanocomposite photocatalysts applied in the photocatalytic water splitting.

**Keywords:** Organic-inorganic hybrid; Tinatia; β-cyclodextrin; Photocatalytic H$_2$-production

**Received** 25 August 2018, **Accepted** 29 November 2018

**DOI:** 10.30919/esmm5f168

### 1. Introduction

Photocatalytic water splitting of hydrogen production is an attractive way for utilization of inexhaustible and clean solar energy.$^1$ Many photocatalysts have been used to improving the hydrogen production of water splitting, especially heterostructured nanoparticles play an important role in photocatalytic water splitting due to the advantages of improving the quantum yield, inhibiting photo-generated carriers recombination and providing reaction active sites, etc. In the last years many hybrid catalysts have been designed and applied for photocatalytic hydrogen production.$^{2-5}$

TiO$_2$ nanoparticles (NPs) have been extensively investigated as promising state-of-the-art photocatalysts due to their strong oxidizing power, non-toxic and simple synthesis.$^1$ However, the poor adsorption performance, low cycle utilization and difficult recycling also limited its application.$^6$ In recent years, many methods have been used to improve the photocactivity of TiO$_2$, such as metal loading, dye sensitization, composite semiconductor, and anion doping.$^6-17$ But it is found that these methods are not effective routes to improve the photocatalytic water splitting of TiO$_2$ nanoparticles. Moreover, as an efficient co-catalysts, noble metals or noble oxides are commonly used in photocatalytic hydrogen generation due to their promotional effect on electron-hole pair separation. However, the high cost and scarcity of noble metals hampered their application in the water splitting of hydrogen production.$^{18-20}$

Hybrid organic-inorganic materials (HOIMs) aroused wide concern due to their inherent advantages of structure. One of the appealing feature for HOIMs is their unique property which is difficult to achieve in either inorganic material or organic material alone.$^{21,22}$ Compared with homogenous materials, the emerging organic-inorganic material have the advantages of dimensional stability which is stemming from the organic phase, as well as the reliability and high catalytic performance which is deriving from the inorganic phase.$^{22-24}$ Although a variety of organic-inorganic materials have been synthesized with superior performance, it is still hard to realize controllable synthesis, and the special heterogeneous structure is difficult to synthesis. Meanwhile, using cyclodextrin (CD) to modify nanomaterial caused concern because it can provide a stable skeleton structure for nanomaterial, and easy to form a unique heterostructure.$^{25}$ Nanomaterial can be endowed with cyclodextrin structure after by modification with CD, which result in more efficient functions and guest-targeting of the TiO$_2$ for cyclodextrin, and cyclodextrin play a role as a "bridge” and “channel” on the surface of the TiO$_2$ nanomaterial.$^{25}$

In this work, a kind of alveolate TiO$_2$/β-cyclodextrin (TiO$_2$/β-CD) organic-inorganic hybrid nano-material has been developed. Notably, the novel TiO$_2$/β-CD nano photocatalyst exhibits outstanding performance on photocatalytic H$_2$ generation. It also exhibits extremely high cycle performance and recyclability. The recyclability of the TiO$_2$/β-CD photocatalyst was found to be no obvious decrease with the H$_2$ generation after third successive runs. We conclude that this alveolate TiO$_2$/β-CD organic-inorganic hybrid nano-material could be expected to be applicable in photocatalytic H$_2$ generation due to the
advantages of strong adsorption, simple synthesis procedure and high cycle utilization performance.

2. Experimental

β-cyclodextrin was recrystallized twice and then dried before use. All other chemicals were of the analytical grade and used without further purification. Tetraethyl orthotitanate (20 ml) was added in deionized water (100 ml) dropwise with vigorous stirring. The solutions were stirred for 24 hours at room temperature (25 °C). And then the white precipitate was washed with deionized water and separated from the liquid phase by centrifugation. The product was dried at 80 °C overnight and ground into powders. The titania (2 g) and β-CD (2 g) were added in deionized water (150 ml) with vigorous stirring. After homogenization for several hours, the mixed solution obtained was transferred into a teflon-lined autoclave for crystallization at 160 °C for 12 h. The resulting product was washed with deionized water by centrifugation. The final product was dried at 80 °C for 12 hours.

3. Results and Discussion

The procedure for synthesis of TiO₂/β-CD organic-inorganic hybrid nano-material was depicted in Fig. 1a. XRD patterns of TiO₂/β-CD nano-material are presented in Fig. 1b. The XRD analysis of hybrid reveals that the nano-material exhibits single-phase which belongs to anatase-type TiO₂, it is identified by comparing the above spectra with the JCPDS file #21-1272. Diffraction peaks at 25.28°, 37.80°, 48.05°, 53.89°, 55.06° and 62.69°, which is corresponding to (101), (004), (200), (105), (211) and (204) planes of TiO₂, respectively. The relatively high intensity of the peak for (101) plane is an indicative of anisotropic growth, implying a preferred orientation of the crystallites. Meanwhile, the synthesized TiO₂/β-CD samples presented XRD patterns similar to pure TiO₂, there is no obvious characteristic peak of β-CD could be found, implying highly uniform dispersion β-CD nanoparticles in TiO₂ matrix. The similar result is also reported by Zhang et al.

The TiO₂/β-CD hybrid nano-material was studied by FE-SEM to research its structure and morphology, as shown in the Fig. 2. The image revealed that TiO₂/β-CD has an alveolate heterogeneous structure with similar aperture of 40 nm. This kind of porous structure is easy to provide more active sites for the photocatalytic performance, and there are many spatial distribution of the hydroxyl groups in the β-CD structure, Thus β-CD could help a lot in capturing the photo generated carriers.

The photocatalytic water splitting of hydrogen evolution activity over pure TiO₂ and TiO₂/β-CD samples was evaluated under visible light illumination (λ > 420 nm). Fig. 3a shows a typical time course of hydrogen evolution for the photocatalytic water splitting of the prepared samples. Stoichiometric evolution of hydrogen is evident from the start of the reaction, and there is a steady hydrogen increase throughout the entire run. TiO₂/β-CD has significantly higher H₂ evolution rates of 5800 μmol/g, which demonstrates it is quite effective to employ β-CD as

![Fig. 1](image1.png)

Fig. 1 (a) Schematic diagram of the synthesis of TiO₂/β-CD organic-inorganic hybrid nano-material (b) X-ray powder diffraction patterns of TiO₂/β-CD.

![Fig. 2](image2.png)

Fig. 2 FE-SEM of the TiO₂/β-CD sample.
catalyst for improving efficiency of TiO₂ photocatalytic activity. With no observable photocatalyst activity decay, Fig. 3b shows the stability of photocatalytic H₂ evolution using the TiO₂/β-CD photocatalyst as the representative sample. The recyclability of the TiO₂/β-CD photocatalyst was found to be high with the H₂ generation at 70% of the initial value after three cycles, revealing the superior long-term stability of TiO₂/β-CD nanocomposites.

The oxidation level for H₂O to H₂O₂ or O₂ is above the valence band (VB), and the conduction band (CB) is higher than the reduction level of hydrogen.34,35 These bands respectively are easily to allow migration of photo-induced holes and electrons of photocatalytic water splitting.34 In this study, we used hydrothermal synthesis method to prepare TiO₂/β-CD hybrid organic-inorganic structure, so it is easy to form binding between cyclodextrin and TiO₂ surface due to the adhesion of the hydroxyl functional groups on the surface. Cyclodextrin would capture holes on active TiO₂ surface resulting in the formation of stable organic-inorganic hybrid composites. The other hand, β-CD could play a role as “bridge” or “channel” for capturing more photo-induced electrons and light, and also provide a larger area for reaction. When TiO₂/β-CD organic-inorganic structure is irradiated by solar light, electrons will be photoexcited into the conduction band (CB), this process will result in the generation of holes on the valence band (VB).

In the presence of β-CD, the photo-induced electrons will quickly transfer to the CB of TiO₂ rapidly, and the H⁺ of water will be reduced into H₂. The result implying that the role of cyclodextrin on TiO₂ nanoparticle acts not only as a molecular transfer channel but also as an electron donator. The synergy between TiO₂ and β-CD is in favor of the energy transfer from the TiO₂ to the β-CD and lead to a high photocatalytic activity.37 Hence, the photocatalytic water splitting of TiO₂/β-CD for hydrogen production are remarkably improved under the condition of solar light irradiation.

The hydrogen/oxygen generation of the basic principle of photocatalytic reactions is depicted in the Fig. 4. In the process of photocatalytic water splitting, the e⁻/h⁺ pairs photogenerated on the TiO₂ particles will move to the β-CD surface where the redox reaction will take place under the photoexcitation process. The oxidation of water is slow than the speed of oxidation of methanol. On the oxidative side, the Ti–OH groups of the β-CD surface will react with the photogenerated holes which result in producing trapped holes, in another way, β-CD may adsorb water molecules and form adsorbed OH radicals. Moreover, it seems indicate that methanol may play an important role in the production of hydrogen production. Sometimes it seems difficult to calculate the exact source of the protons yielding H₂ from methanol or water, or rather whether source of H⁺ is belonged to water or CH₃OH.

![Fig. 3](image1.png)

**Fig. 3** (a) Hydrogen evolution of the samples under the xenon lamp irradiation (b) Cycling runs for the photocatalytic hydrogen evolution.

![Fig. 4](image2.png)

**Fig. 4** The basic principle of photocatalytic reactions for hydrogen/oxygen generation using electron donors/acceptors as the sacrificial reagent.
4. Conclusion
In this work, we demonstrated a kind of TiO$_2$/$\beta$-CD organic-inorganic hybrid nano-material with alveolate structure via a facile one-step strategy in low temperature. Because of its better adsorption capability, efficient separation and migration of photo-induced electron-hole pairs and larger BET surface area, the supramolecular TiO$_2$/$\beta$-CD hybrid exhibited considerably enhanced photocatalytic activity and good cycle performance towards the H$_2$ evolution. This TiO$_2$/$\beta$-CD nano photocatalyst could be expected to be applicable in photocatalytic water splitting under solar light due to its merits of simple procedure, recyclability and high catalytic activity. And it opens up new possibilities and opportunities for developing other hybrid organic-inorganic materials by incorporating a large array of organic materials for a variety of technological applications in the solar hydrogen production or environmental cleaning.

Acknowledgements
This work was supported by the Fundamental Research Funds for the Central Universities (DL11EB02), the National Natural Science Foundation of China (51508293), China Postdoctoral Science Foundation Funded Project (2016M600527), and Science and Technology Development Fund from Macau (FDCT-010/2017/AMJ). The China Ministry of Science and Technology under Grant 2015CB655100, and Major International Joint Research Project under Grant 51420105015 are gratefully acknowledged. The first author also would like to acknowledge the fellowship support received from the Tai Shan Scholar Program.

References
4. X. Xia, S. Peng, Y. Bao, Y. Wang, B. Lei, Z. Wang, Z. Huang, Y. Gao, J. Power Sources, 2018, 376, 11-17.
20. S. Guo, T. Zhao, J. Quan, S. Han, J. Power Sources, 2015, 293, 17-22.
32. X. Zhang, F. Wu, N. Deng, J. Hazard Mater., 2011, 185, 117-123.