



TiO₂/Cyclodextrin Hybrid Structure with Efficient Photocatalytic Water Splitting

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A novel TiO₂/β-cyclodextrin (TiO₂/β-CD) organic-inorganic hybrid nano-material with alveolate structure is fabricated using a facile one-step strategy. The alveolate TiO₂/β-CD hybrid nano-material exhibits outstanding photocatalytic activity and recyclability on photocatalytic water splitting. The production of H₂ evolution of TiO₂/β-CD hybrid reaches to 5800 μmolg⁻¹ after 8 h without noble metal. Meanwhile, the recyclability of the TiO₂/β-CD photocatalyst is found to be no obvious decrease with the H₂ 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 TiO₂ could be the predominant active species in the photocatalytic system. Due to the alveolate heterogeneous structure of TiO₂/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.

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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.^{2,4}

TiO₂ nanoparticles (NPs) have been extensively investigated as promising state-of-the-art photocatalysts due to their strong oxidizing power, non-toxic and simple synthesis.⁵ However, the poor adsorption performance, low cycle utilization and difficult recycling also limited its application.^{6,7} In recent years, many methods have been used to improve the photoactivity of TiO₂, such as metal loading, dye sensitization, composite semiconductor, and anion doping.⁸⁻¹⁷ But it is found that these methods are not effective routes to improve the photocatalytic water splitting of TiO₂ 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 electrone-hole pair separation. However, the high cost and scarcity of noble metals hampered their application in the water splitting of hydrogen production.^{7,18-20,29}

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 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.²²⁻²⁶ 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.²⁷ Nanomaterial can be endowed with cyclodextrin structure after by modification with CD, which result in more efficient functions and guest-targeting of the TiO₂ for cyclodextrin, and cyclodextrin play a role as a "bridge" and "channel" on the surface of the TiO₂ nanomaterial.²⁸

In this work, a kind of alveolate TiO₂/β-cyclodextrin (TiO₂/β-CD) organic-inorganic hybrid nano-material has been developed. Notably, the novel TiO₂/β-CD nano photocatalyst exhibits outstanding performance on photocatalytic H₂ generation. It also exhibits extremely high cycle performance and recyclability. The recyclability of the TiO₂/β-CD photocatalyst was found to be no obvious decrease with the H₂ generation after third successive runs. We conclude that this alveolate TiO₂/β-CD organic-inorganic hybrid nano-material could be expected to be applicable in photocatalytic H₂ generation due to the

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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. Tetrabutyl 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 $\text{TiO}_2/\beta\text{-CD}$ organic-inorganic hybrid nano-material was depicted in Fig. 1a. XRD patterns of $\text{TiO}_2/\beta\text{-CD}$ 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 TiO_2 , 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 TiO_2 , respectively.²⁹ 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 $\text{TiO}_2/\beta\text{-CD}$ samples presented XRD patterns similar to pure TiO_2 , there is no obvious characteristic peak of $\beta\text{-CD}$ could be found, implying highly uniform dispersion $\beta\text{-CD}$ nanoparticles in TiO_2 matrix. The similar result is also reported by Zhang *et al.*³⁰

The $\text{TiO}_2/\beta\text{-CD}$ hybrid nano-material was studied by FE-SEM to research its structure and morphology, as shown in the Fig. 2. The image revealed that $\text{TiO}_2/\beta\text{-CD}$ 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 $\beta\text{-CD}$ structure. Thus $\beta\text{-CD}$ could help a lot in capturing the photo generated carriers.³³

The photocatalytic water splitting of hydrogen evolution activity over pure TiO_2 and $\text{TiO}_2/\beta\text{-CD}$ samples was evaluated under visible light illumination ($\lambda > 420$ 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. $\text{TiO}_2/\beta\text{-CD}$ has significantly higher H_2 evolution rates of 5800 $\mu\text{mol/g}$, which demonstrates it is quite effective to employ $\beta\text{-CD}$ as

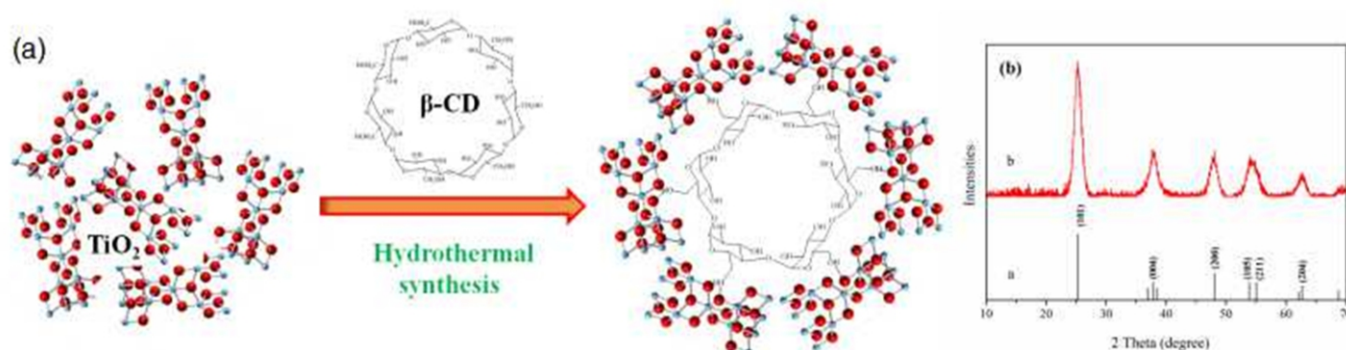


Fig. 1 (a) Schematic diagram of the synthesis of $\text{TiO}_2/\beta\text{-CD}$ organic-inorganic hybrid nano-material (b) X-ray powder diffraction patterns of $\text{TiO}_2/\beta\text{-CD}$.

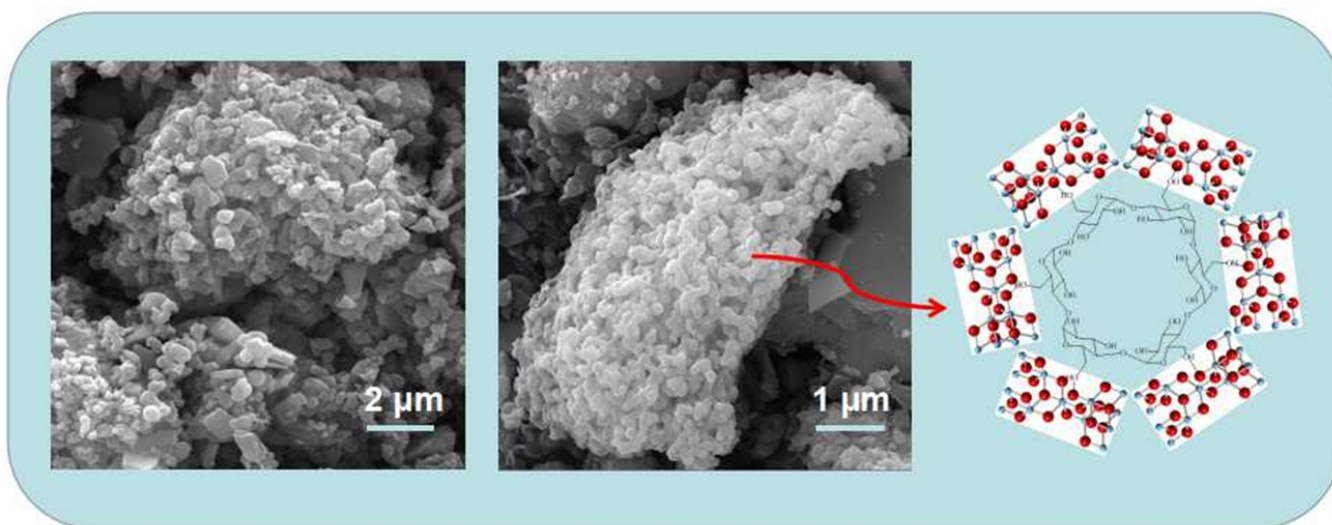


Fig. 2 FE-SEM of the $\text{TiO}_2/\beta\text{-CD}$ sample.

cocatalyst for improving efficiency of TiO_2 photocatalytic activity. with no observable photocatalyst activity decay. Fig. 3b shows the stability of photocatalytic H_2 evolution using the $\text{TiO}_2/\beta\text{-CD}$ photocatalyst as the representative sample. The recyclability of the $\text{TiO}_2/\beta\text{-CD}$ photocatalyst was found to be high with the H_2 generation at 70 % of the initial value after third cycles, revealing the superior long-term stability of $\text{TiO}_2/\beta\text{-CD}$ nanocomposites.

The oxidation level for H_2O to H_2O_2 or O_2 is above the valence band (VB), and the the conduction band (CB) is high 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.³⁶ In this study, we used hydrothermal synthesis method to prepare $\text{TiO}_2/\beta\text{-CD}$ hybrid organic-inorganic structure, so it is easy to form binding between cyclodextrin and TiO_2 surface due to the adhesion of the hydroxyl functional groups on the surface. Cyclodextrin would capture holes on active TiO_2 surface resulting in the formation of stable organic-inorganic hybrid composites. On the other hand, $\beta\text{-CD}$ 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 $\text{TiO}_2/\beta\text{-CD}$ 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 $\beta\text{-CD}$, the photo-induced electrons will quickly transfer to the CB of TiO_2 rapidly, and the H^+ of water will be reduced into H_2 . The result implying that the role of cyclodextrin on TiO_2 nanoparticle acts not only as a molecular transfer channel but also as an electron donor. The synergy between TiO_2 and $\beta\text{-CD}$ is in favor of the energy transfer from the TiO_2 to the $\beta\text{-CD}$ and lead to a high photocatalytic activity.³⁷ Hence, the photocatalytic water splitting of $\text{TiO}_2/\beta\text{-CD}$ 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 TiO_2 particles will move to the $\beta\text{-CD}$ surface where the redox reaction will take place under the photoexcitation progress. The oxidation of water is slow than the speed of oxidation of methanol. On the oxidative side, the Ti-OH groups of the $\beta\text{-CD}$ surface will react with the photogenerated holes which result in producing trapped holes, in another way, $\beta\text{-CD}$ 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 H_2 from methanol or water, or rather whether source of H^+ is belonged to water or CH_3OH .

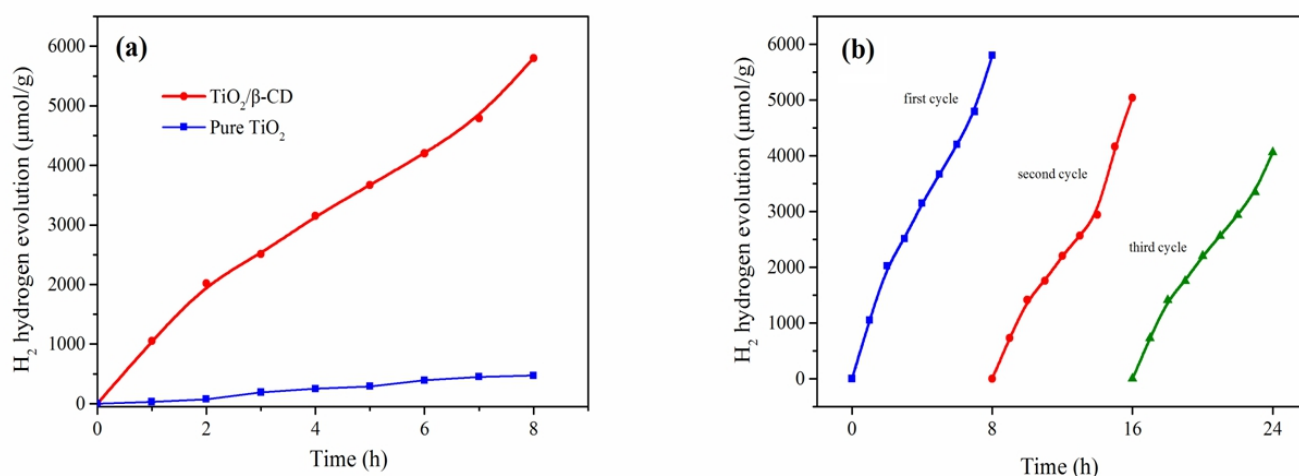


Fig. 3 (a) Hydrogen evolution of the samples under the xenon lamp irradiation (b) Cycling runs for the photocatalytic hydrogen evolution.

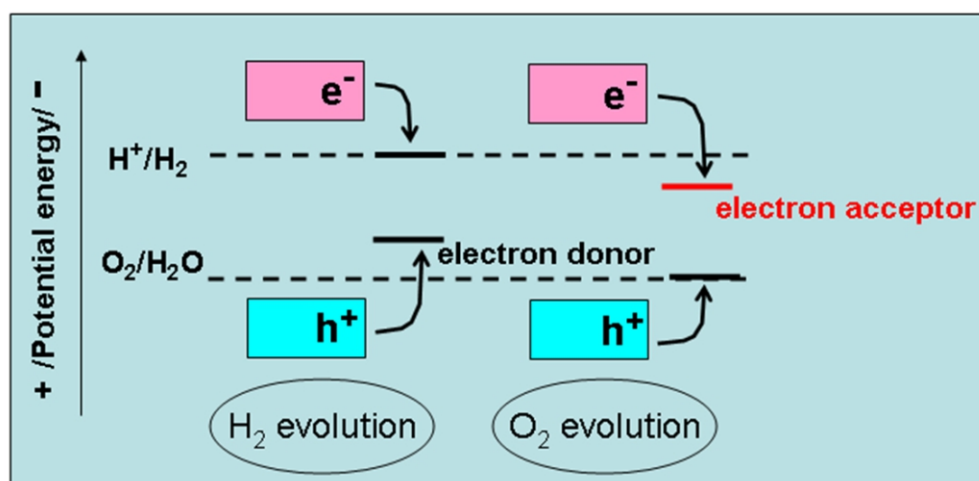


Fig. 4 The basic principle of photocatalytic reactions for hydrogen/oxygen generation using electron donors/acceptors as the sacrificial reagent.

4. Conclusion

In this work, we demonstrated a kind of $\text{TiO}_2/\beta\text{-CD}$ 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 $\text{TiO}_2/\beta\text{-CD}$ hybrid exhibited considerably enhanced photocatalytic activity and good cycle performance towards the H_2 evolution. This $\text{TiO}_2/\beta\text{-CD}$ 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.

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