INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 38 (2013) 8639–8647

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/he

Efficient photochemical hydrogen production under visible-light over artificial photosynthetic systems

Jianjun Chen [a], *Huilan Su* [a,*], *Yujia Liu* [a], *Yiwei Zeng* [a], *Wang Zhang* [a], *Jiajun Gu* [a], *Woon Ming Lau* [b,c], *Di Zhang* [a,*]

[a] *State Key Lab of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, PR China*
[b] *Chengdu Green Energy and Green Manufacturing Technology R&D Center, Chengdu, Sichuan 610207, PR China*
[c] *Beijing Computational Science Research Center, Beijing 100084, PR China*

ARTICLE INFO

Article history:
Received 25 February 2013
Received in revised form
3 May 2013
Accepted 6 May 2013
Available online 7 June 2013

Keywords:
$CdS/Pt{-}TiO_2$
Reticular hierarchical structure
Artificial photosynthetic systems
Hydrogen production

ABSTRACT

Photosynthesis of green plants provides an effective blueprint for transform solar energy into useful hydrogen energy. Thereinto, their hierarchical structures are favorable to the light-harvesting. Meanwhile, the functional components (light-harvesting pigments) can absorb visible wavelengths of sunlight, and offer reaction center for the energy transform. Inspired by these, we contrive an artificial photosynthetic system for the high efficiency of H_2-production rate by introducing a similar functional structure (reticular hierarchical structure) and component ($CdS/Pt{-}TiO_2$). The $CdS/Pt{-}TiO_2$ with hierarchically reticular structure is prepared by transforming wings into TiO_2 via a sol–gel process, and depositing Pt and CdS nanoparticles onto the TiO_2 substrate by photoreduction and chemical bath deposition method, respectively. Contributing to the couple effect of reticular hierarchical structure and ternary hybrid composition, $CdS/Pt{-}TiO_2$ nanocomposites exhibit high visible-light photocatalytic H_2-production rate (12.7% apparent quantum efficiency obtained at 420 nm). This concept provides a new horizon to exploit solar energy for sustainable energy by imitating the photosynthesis process from structure and ingredients.

1. Introduction

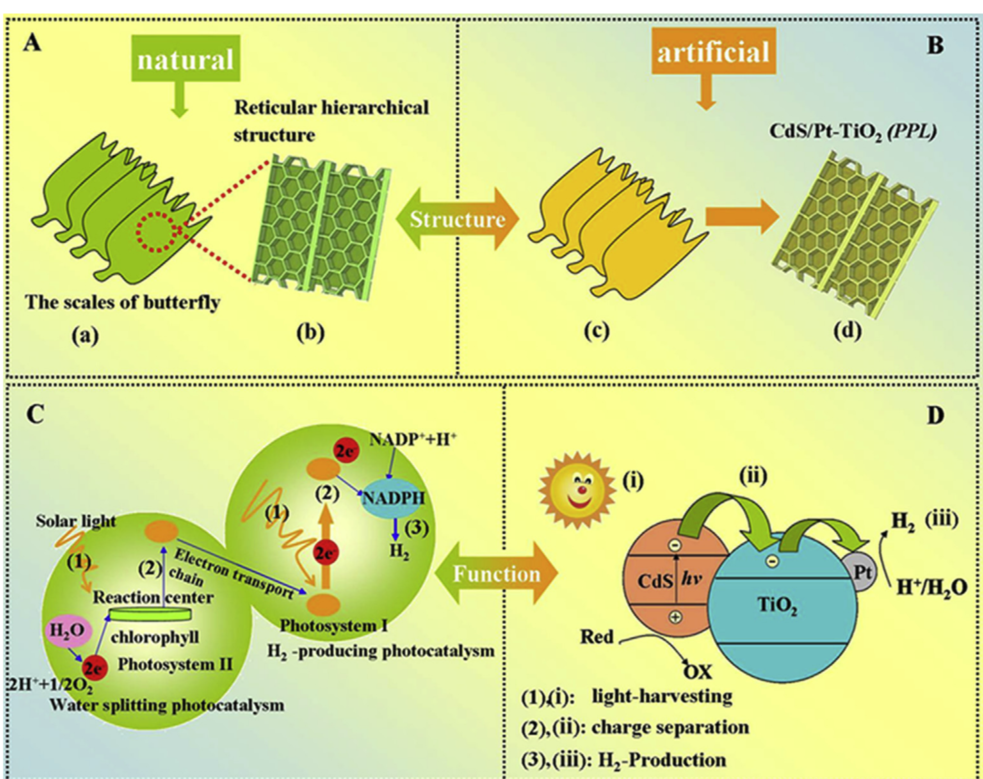
The increasing environmental problem and limited oil reserve have led to a new focus on the development of clean and renewable hydrogen energy sources. Sunlight driven water splitting for hydrogen generation provides a promising strategy to transform solar energy into valuable hydrogen energy. Since Fujishima and Honda demonstrated that TiO_2 could split water to produce H_2 [1], TiO_2 has been widely studied for water splitting due to its low cost nontoxicity and good stability. Nevertheless, the solar-to-hydrogen energy conversion efficiency of TiO_2 needs further improvement due to its large band gap (3.2 eV) and the quick recombination of photo-induced electron–hole pairs. In the past few years, plenty of efforts have been made to enhance its photocatalytic efficiency by modifying the composition [2–7] and structures [8–11]. Although significant progress has been made, the solar-to-hydrogen energy conversion efficiency is still too low to meet practical applications. Nature provides us an inspiration to solve this problem. The photosynthetic system of green plants can capture solar energy and split water into "hydrogen" efficiently. On one hand, its hierarchical structure

* *Corresponding authors.* Tel.: +86 21 34202584; fax: +86 21 34202749.
E-mail addresses: hlsu@sjtu.edu.cn (H. Su), zhangdi@sjtu.edu.cn (D. Zhang).
0360-3199/$ – see front matter
http://dx.doi.org/10.1016/j.ijhydene.2013.05.045

can bring about multiple scattering and provide strong light-harvesting for photosynthesis [12]. On the other hand, the biologic functional components (light-harvesting pigments) can absorb visible light, transfer the excitation energy to special locations, and facilitate charge-separation for the subsequent solar energy conversion (Scheme 1C) [13]. Thus, building artificial photosynthetic systems with analogous functional structure and ingredient might provide another route to improve the solar-to-hydrogen energy conversion efficiency.

According to the previous report, the hierarchical structures of green leaves can provide strong light-harvesting for photosynthesis by multiple scattering [14]. In practice, architecture of leaves is complicated and it needs a complex pretreatment and synthesis procedure to preserve its fine hierarchical structures. This limitation motivates us to search for an even more facile structure to substitute the function of leaf-shaped architecture. Thereinto, the black scales of butterfly wings (*Papilio Paris Linnaeus*) with hierarchically reticular structure have got our attention. The subtle structure of the black scales is shown in Fig. 1b–d. A typical scale (Fig. 1b) consist of an upper layer and a simple bottom layer (Fig. 1d). Periodic ridges run the length of these scales on the upper layer (Fig. 1c). Between the ridges, scales present an aperiodic porous structure, which is denoted as "reticulum structure" (Scheme 1b). The average hole diameter is about 650 nm. The ridging, aperiodic porous structure and bottom layer are responsible for the light-harvesting of the butterfly wings [15]. That is, the ridges on the upper layer reflect and guide the light into the reticular structure arrays. When the light enters the reticular structure, multiple scattering happens which can enhance the optical path length. Meanwhile, the light escaping from the reticulum structure is reflected back by the bottom layer. A high rate of light-harvesting is obtained by cyclic reflection and scattering. Therefore, the function of leaf-shaped hierarchical structure can be substituted with the black scales of butterfly wings (*Papilio Paris Linnaeus*). In our previous work, Pt/TiO_2 with the artificial butterfly wing architecture was generated to improve photocatalytic efficiency [16]. Nevertheless, it only presented enhanced the hydrogen evolution rate under UV light owing to its large band gap. Thus, Pt/TiO_2 cannot replace the role of light-harvesting pigments whose absorbing wavelengths are mainly in visible light range. In this report, multi-semiconductor systems have been introduced to solve this problem. Depositing CdS nanocrystallites onto the Pt-loaded TiO_2 (CdS/Pt–TiO_2) not only presents superior visible light-harvesting capability, but also possesses high charge separation efficiency [17–20], which is similar to the function of light-harvesting pigments. Integratively, it is possible to realize artificial photosynthesis by endowing CdS/Pt–TiO_2 with reticular hierarchical structure of butterfly wings.

Herein, the artificial photosynthetic systems are to be constructed to enhance hydrogen production under visible light by introducing the reticulum hierarchical structure of butterfly wings, and replacing the natural functional components with man-made CdS/Pt–TiO_2 catalysts. The TiO_2 with reticular hierarchical structure is firstly prepared by a sol–gel process combined with subsequent calcination, and then Pt and CdS nanoparticles can be deposited onto TiO_2 by



Scheme 1 – (A) The hierarchical structures of butterfly wings, (B) the artificial ternary photocatalyst, (C) natural photosynthesis process, (D) a possible photocatalytic mechanism in the artificial ternary photocatalyst.