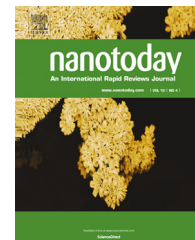




Available online at www.sciencedirect.com

ScienceDirect

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



REVIEW

Solar fuel production: Strategies and new opportunities with nanostructures



Zhaosheng Li^{a,b,*}, Jianyong Feng^{a,b}, Shicheng Yan^{a,b},
Zhigang Zou^{a,b,*}

^a Collaborative Innovation Center of Advanced Microstructures, National Laboratory of Solid State Microstructures, College of Engineering and Applied Sciences, 22 Hankou Road, Nanjing 210093, People's Republic of China

^b Jiangsu Key Laboratory for Nano Technology, Nanjing University, 22 Hankou Road, Nanjing 210093, People's Republic of China

Received 15 February 2015; received in revised form 27 May 2015; accepted 18 June 2015

Available online 15 July 2015

KEYWORDS

Photocatalysts;
Photoelectrodes;
Water splitting;
Nanostructure;
CO₂ photoreduction;
Atomic layer
deposition

Summary The photocatalytic and photoelectrochemical reduction of water or CO₂ is an intriguing approach to producing sustainable solar fuels, and has attracted growing and intense interest. Nanostructuring of photocatalysts and photoelectrodes has been proven to be a strong strategy to dramatically improve overall solar-to-fuel conversion efficiencies. Another technological barrier for the practical implementation of solar fuel production is long-term material durability, which has recently been well addressed through use of conformal coatings of protective layers onto the narrow band-gap semiconductors that are suitable for efficient solar-to-fuel conversions but photoelectrochemically unstable. These significant progresses may lead us to the practical implementation of solar fuel production. In this review, we will focus on these exciting progresses achieved using nanostructuring strategies, specifically regarding how the nanostructure influences the charge transport and separation; special attention will be paid to how a nanoscale coating (overlayer) passivates the surface states, thereby reducing the surface electron–hole recombination, and how a nanoscale coating (protective layer) prevents the photocorrosion or photopassivation of the semiconductors with optimal band gaps. We hope that the design strategies using these nanostructures will offer new and greater opportunities for efficient solar fuel production to existing photocatalytic and photoelectrochemical systems.

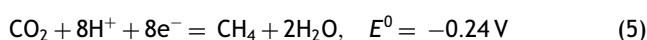
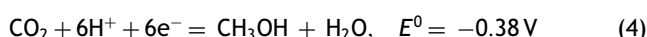
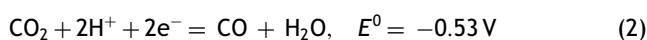
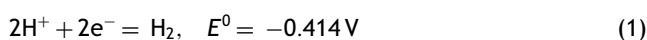
© 2015 Elsevier Ltd. All rights reserved.

* Corresponding authors at: Collaborative Innovation Center of Advanced Microstructures, National Laboratory of Solid State Microstructures, College of Engineering and Applied Sciences, 22 Hankou Road, Nanjing 210093, People's Republic of China. Tel.: +86 25 83686304x800; fax: +86 25 83686632.

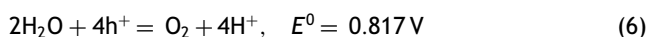
E-mail addresses: zqli@nju.edu.cn (Z. Li), zgrou@nju.edu.cn (Z. Zou).

Introduction

Powering our society with clean and renewable energy is an important mission, particularly due to the growing consumption of fossil energy and the increasing content of CO₂ in the atmosphere. Solar fuel production using sunlight-to-chemical energy conversions is a potential and promising approach to generate transportable and renewable energy [1–5]. The fuel-forming process can be realized through the photocatalytic or the photoelectrochemical (PEC) reduction of H₂O to H₂ (solar-to-hydrogen conversion) or CO₂ to hydrocarbons (solar-to-hydrocarbon conversion), which are also referred to as artificial photosynthesis [6–8]. The thermodynamic requirements for fuel-forming reductive reactions are described as follows (pH 7 in an aqueous solution vs. a normal hydrogen electrode, 25 °C, 1 atm gas pressure, and 1 M for other solutes) [9,10]:



Ideally, the corresponding oxidative half-reaction is the oxidation of H₂O to O₂:



High efficiency is a prerequisite for the practical application of solar-to-fuel conversion. The theoretical solar-to-fuel conversion efficiency of a semiconductor (photocatalyst or photoelectrode) is largely determined by its band structure. Narrow band-gap semiconductor photocatalysts or photoelectrodes are one prerequisite to achieve high solar-to-fuel conversion efficiency, and have consequently drawn a great deal of attention. For example, n-Si, n-CdTe, Ta₃N₅, hematite, BaTaO₂N, and LaTiO₂N photoanodes exhibit high photoelectrochemical performance for water oxidation [11–17], while p-InP, p-Si, CuIn_{1-x}Ga_xSe₂, and p-WSe₂ photocathodes are promising for water reduction [18–21].

Another prerequisite for achieving high solar-to-fuel conversion efficiency is efficient charge separation and rapid surface reaction rates in semiconductors. Strategies of nanostructuring the semiconductors have offered favorable and continuous improvement in solar-to-fuel conversion efficiency [22–28]. Compared to their bulk counterparts, the following unique features that belong to nanostructured semiconductors provide the possibility and the means to improve overall solar-to-fuel conversion efficiency:

(1) *Shortened carrier collection pathway.* The most significant merit associated with nanostructures is the ability to match the characteristic dimension to the collection length of photoexcited charge carriers, which is often on the order of tens of nanometers [26]. In the case of the particle photocatalyst system for solar-to-fuel conversion, the photogenerated carriers must transfer to the photocatalyst surface before they take part in the subsequent redox reactions. In order to

drive the redox reactions in the photoelectrode system, the photogenerated minority and majority carriers are required, respectively, to reach the photoelectrode/electrolyte interface and the counter electrode. Shorter carrier collection pathways imply reduced transfer times for charge carriers through the semiconductor bulk; therefore, shortened carrier collection pathways through nanostructuring of semiconductors are potentially beneficial to reduce the recombination probability of electron–hole pairs [29].

(2) *Enlarged specific surface area.* Another direct result of nanostructuring photocatalysts or photoelectrodes is the drastic increase of their specific surface areas. The enlarged specific surface area immediately exhibits a strong effect for improving surface reaction rates by enhancing the adsorption of reactant molecules of H₂O or CO₂ [30–32]. In the case of the PEC system for solar-to-fuel conversion, the enlarged specific surface area of nanoporous photoelectrodes also allows the local current density to be much smaller than what is required for bulk photoelectrodes, thus relaxing the constraints on the interfacial kinetics and reducing the required overpotential [26]. As proposed by Lewis et al., this may allow for the utilization of earth-abundant electrocatalysts with lower activities that could replace highly active precious metal based electrocatalysts [2].

(3) *Increased volume ratio of space charge layer to bulk.* Reducing the feature size of the semiconductors is a general strategy to effectively increase the volume ratio of the space charge layer to semiconductor bulk. Taking the PEC system as an example, assuming the widths of the space charge layers within the semiconductors are identical for nanostructured and planar electrodes when they come in contact with electrolytes, the nanostructured electrode will produce a greater volume of space charge layer than the planar electrode. This is because the former forms a broader area of electrolyte/semiconductor interface (the space charge layer within the semiconductor) than the latter does. The space charge layer promotes the electrons and holes to the conductive substrate and the electrolyte/semiconductor junction (taking the n-type photoelectrode as an example), respectively, with high efficiency. Therefore, increasing the volume ratio of the space charge layer to bulk through nanostructuring is an efficient strategy to enhance the separation of charge carriers thereby improving solar-to-fuel conversion efficiency. One should note, however, when the semiconductor is smaller than its critical size, the semiconductor will be fully depleted when it comes in contact with electrolytes, and the thickness of the space charge layer will become thinner or possibly disappear [23]. Under this condition, the charge carriers transport by diffusion instead of drift, leading to increased chances for charge carrier recombination and back reactions [33].

(4) *Enlarged band gap (accompanying the shift of conduction or/and valance band edge).* Due to the quantum size effect (confinement of electronic structures to small regions of space in one, two, or three dimensions), one unusual property of extremely small semiconductor nanocrystals is that their band gaps become larger,

Download English Version:

<https://daneshyari.com/en/article/32069>

Download Persian Version:

<https://daneshyari.com/article/32069>

[Daneshyari.com](https://daneshyari.com)