available at www.sciencedirect.com

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

Communication (Special Issue of Photocatalysis for Solar Fuels)

Synthesis of PdS-CdSe@CdS-Au nanorods with asymmetric tips with improved H₂ production efficiency in water splitting and increased photostability

Xianmei Xiang, Lingjun Chou, Xinheng Li *

State Key Laboratory for Oxo Synthesis and Selective Oxidation and Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Suzhou 215123, Jiangsu, China

ARTICLE INFO

Article history:

Received 25 September 2017

Accepted 30 October 2017

Published 5 March 2018

Keywords:

Photocatalysis

Charge separation

Cocatalyst

Heterostructure

Water splitting

ABSTRACT

Charge separation is a crucial problem in photocatalysis. We used a wet-chemical method to synthesize asymmetrically tipped PdS-CdSe-seeded CdS (CdSe@CdS)-Au nanorod (NR) heterostructures (HCs). In these HCs, electrons and holes are rapidly separated and transported to opposite ends of the NRs by internal electric fields. Their ultraviolet-visible absorption spectra showed strong electronic coupling between both tips and the CdS body. PdS-CdSe@CdS-Au achieved a H₂ production rate of ca. 1100 μmol in 5 h; this is two orders of magnitude greater than the rate achieved with Au-CdSe@CdS NRs with only one tip. PdS-CdSe@CdS-Au NRs can withstand 4 h of photoirradiation, compared to 1.5 h for CdSe@CdS NRs, indicating that the photostability of PdS-CdSe@CdS-Au is much better than that of CdS. The greatly improved photocatalytic activity and stability are attributed to efficient charge separation and rapid charge transport in the PdS-CdSe@CdS-Au HCs.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.
Published by Elsevier B.V. All rights reserved.

Photocatalysts such as heterostructured photocatalysts have shown promise for use in environmental remediation and water splitting [1,2]. In heterostructured photocatalysts, which are produced by incorporating cocatalysts into narrow band gap semiconductors, the internal electric field that can build up at the interface can be used to rapidly break up electron/hole pairs, thereby enhancing the solar-to-fuel conversion efficiency [3]. Li et al. [4–6] reported that dual cocatalysts consisting of Pt and PdS on CdS achieved the highest quantum efficiency (93%) obtained to date in H₂ production by water splitting. Grätzel et al. [7] immobilized a molecular cocatalyst on Cu₂O to produce a photocathode for CO₂ reduction, effectively enhancing the solar-to-fuel conversion efficiency. Nanocrystalline semiconduc-

tors such as CdS have advantages such as controllable well-defined geometric structures, few body and surface defects, and large surface areas [8]. These have been widely studied in recent decades [9–11] but the precise synthesis of sophisticated CdS heterostructures (HCs) with controllable well-defined structures is still a challenge. CdS suffers from severe photo-erosion [12]. One strategy for tackling such problems is to deposit a protective layer of ultrathin carbon around CdS; this greatly improves the photocatalytic stability and activity [13]. Another strategy is to synthesize HCs such as PbSe-CdS [14], which can pull electrons/holes away from CdS; this protects CdS from photo-erosion and improves the photocatalytic activity. One-dimensional HCs with tipped materials,

* Corresponding author. Tel/Fax: +86-512-81880906; E-mail: xinhengli@licp.cas.cn

This work was supported by the National Key Research and Development Program of China (2016YFE0105700), the National Natural Science Foundation of China (21573263), and Provincial Fundamental Research Plan of Jiangsu (BK20151236).

DOI: 10.1016/S1872-2067(17)62970-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 3, March 2018

such as Au-tipped CdSe-seeded CdS (CdSe@CdS) nanorods (NRs) are of particular interest because the long axis of the rod naturally provides a direct path for charge transport [15]. The production of such structures involves synthesis of semiconductor nanoparticles and subsequent heterogeneous nucleation and growth via a mild deposition process.

In our previous studies, we investigated the deposition of symmetric tips such as a metal (Au), metal oxide (Fe_3O_4), or sulfide (PdS) onto CdS NRs, i.e., the materials deposited on both ends of the NRs are the same [16]. In this process, it is necessary to minimize homogeneous nucleation of the metal precursor and/or Ostwald ripening of the semiconductor particles during deposition. Au-CdS NRs and PdS-CdS NRs show good charge separation [17]. Here, we report the deposition of asymmetric tips, i.e., one tip is Au and the other tip is PdS, on CdSe@CdS NRs. We used the obtained nanostructures in water splitting for H_2 production. The H_2 production efficiency and photocatalytic stability of CdS were greatly enhanced by efficient charge separation.

Scheme 1 shows the procedure for PdS-CdSe@CdS-Au NR synthesis. The synthesis of CdSe-seeded CdS NRs was described in detail in an earlier publication [18]. Au-tipped CdSe@CdS NRs with a match-stick structure were obtained by controlling the concentration of the Au precursor. In a typical synthesis, a HAuCl_4 solution (20 $\mu\text{g/mL}$, 2 mL) and a dodecylamine toluene solution (28 mg/mL, 2 mL) were mixed. A CdSe@CdS NR stock solution ($\sim 50 \mu\text{mol/L}$, 1 mL) was injected into the mixed solution and the reaction was performed for ca. 30 min at room temperature. PdS was then deposited on the other end of the Au-CdSe@CdS NRs by cation exchange. A mixture of CdSe@CdS NR toluene solution (1 mL), oleylamine (2 mL), and oleic acid (1 mL) was rapidly injected into a $\text{Pd}(\text{acac})_2$ precursor solution at 180 $^\circ\text{C}$ and the reaction was continued for ca. 15 min under

Scheme 1. Schematic of synthetic procedures of PdS-CdSe@CdS-Au nanorod heterostructures via heterogeneous deposition and cation exchange methods.

N_2 . The product was transferred into an aqueous solution by ligand exchange with mercaptoundecanal acid and used for water splitting. An aqueous solution of the obtained photocatalyst (100 mL) was placed in a reactor under a 300 W Xe lamp. Na_2S (0.5 mol/L) and Na_2SO_3 (0.5 mol/L) were used as sacrificial reagents. The solution was thoroughly degassed and the amounts of H_2 evolved were determined by gas chromatography with Ar as the carrier gas.

Fig. 1 shows the structural characterization results for the as-synthesized CdSe@CdS NRs, Au-tipped CdSe@CdS NRs with a match-stick structure (Au-CdSe@CdS NRs), and asymmetrically tipped CdSe@CdS NRs (PdS-CdSe@CdS-Au NRs). The CdSe@CdS NRs are ca. 50 nm in length and 4.2 nm in diameter. The NR size is highly monodispersed. The transmission electron microscopy (TEM) image in Fig. 1(b) shows that round Au tips were deposited on one end of the CdSe@CdS NRs with a selectivity of ca. 85% by controlling the concentration of the Au precursor. The energy-filtered transmission electron microscopy (TEM) image in Fig. 1(c) confirms that the majority of the

Fig. 1. TEM image (a) of CdSe@CdS nanorods; TEM image (b) and energy filtered STEM image (c) of Au-CdSe@CdS nanorods; TEM image (d), HRTEM image (e) and EDS spectra (f) of PdS-CdSe@CdS-Au nanorods. Inset images in Fig. 1(b) and (d) are magnification images of the corresponding samples.

CdSe@CdS NRs were decorated with Au on only one tip. The average size of the Au tips is ca. 1.5 nm. Fig. 1(d), (e), and (f) show TEM and high-resolution TEM images, and the energy-dispersive X-ray spectrum (EDS) of PdS-CdSe@CdS-Au NRs. These show that one end of the CdSe@CdS NRs is tipped with PdS, and the other end is tipped with Au. The clearly observed lattice spacing of ca. 0.336 nm is attributed to the (002) plane of the CdS body of the NRs. The lattice spacing of ca. 0.24 nm on the tip is attributed to the (111) plane of crystalline Au. The other tip of the NR clearly differs from the CdS and Au parts; its shape and size differ from those of the Au tip. We performed control experiments (Fig. S1) in which PdS-CdSe@CdS-PdS NRs were synthesized. The PdS tips also lacked of crystalline lines. Metallic Pd would show crystalline lines [16], therefore we conclude that the other tip is PdS; this is in good agreement with the literature [19]. Furthermore, the EDS data in Fig. 1(f) confirm the presence of Pd and S, indicating formation of PdS. After PdS deposition, the length of the CdSe@CdS NRs decreased slightly because of partial cation exchange of CdS with Pd precursors. The selectivity for the PdS-CdSe@CdS-Au NRs was ca. 70%, as shown in Fig. S2. These results show that we successfully synthesized asymmetrically tipped CdSe@CdS NRs, with one Au tip and one PdS tip. Note that although bare CdSe@CdS NRs can be easily synthesized using solvothermal methods, the pyrolysis of metal-organic precursors at a high temperature gives highly crystalline CdSe@CdS NRs.

Fig. 2(a) shows the ultraviolet-visible (UV-Vis) absorption spectra of CdSe@CdS NRs, Au-CdSe@CdS NRs, and PdS-CdSe@CdS-Au NRs. The CdSe@CdS NRs give four distinct absorption bands; the peaks at $\lambda \approx 470$, 430, and 390 nm correspond to the shell CdS, and the weak peak at $\lambda \approx 580$ nm corresponds to the CdSe core. The deposition of Au on only one tip did not greatly change the peaks at $\lambda = 430$ and 380 nm because the volume of Au is small relative to that of the NR body. After deposition of the PdS tip to form asymmetric PdS-CdSe@CdS-Au NRs, the CdS absorption peaks became ambiguous, indicating strong electronic coupling between the CdS shell and its two tipped domains. Fig. 2(b) shows that the CdSe@CdS NRs gave a photoluminescence (PL) peak at $\lambda \approx 597$

nm, with a full width at half maximum of ca. 35 nm. After Au and PdS deposition, the PL intensity decreased to nearly zero because of strong fluorescence quenching by Au and PdS; this indicates that rapid charge separation occurred. Note that the PdS PL peak at $\lambda = 650$ nm was not observed because of the relatively small volume of PdS.

Fig. 3(a) shows the photocatalytic activities of the PdS-CdSe@CdS-Au NRs, Au-CdSe@CdS NRs, and CdSe@CdS NRs. For the CdSe@CdS NRs and Au-CdSe@CdS NRs, the amount of H_2 produced increased linearly with time. The amount of H_2 produced by each sample was ca. 50 μmol in 5 h, and Au-CdSe@CdS gave a slightly better performance than CdSe@CdS. For the PdS-CdSe@CdS-Au NRs, the amount of H_2 produced increased linearly in the first 3 h and then reached a plateau at ca. 1100 μmol at around 5 h. This is more than two orders of magnitude greater than the production achieved by CdSe@CdS and Au-CdSe@CdS. This proves that the asymmetrically tipped PdS-CdSe@CdS-Au NRs had significantly higher photocatalytic activity in water splitting. A plateau is reached because of NR photo-erosion. The TEM images in Fig. 3(b) and 3(c) show photo-erosion tests of the as-obtained PdS-CdSe@CdS-Au NRs and CdSe@CdS. CdSe@CdS was completely destroyed after photoirradiation for 1.5 h, but the PdS-CdSe@CdS-Au NRs retained their shapes and edges even after 4 h of photoirradiation. This clearly proves that the asymmetrically tipped PdS-CdSe@CdS-Au NRs had significantly improved photostability. In H_2 production over a longer period, PdS-CdSe@CdS-Au corroded after 5 h, as shown in Fig. S3, therefore use of the NRs over long periods of time would result in structural damage. In summary, incorporation into asymmetrically tipped PdS-CdSe@CdS-Au NRs significantly improved the photocatalytic activity and photostability of CdS. The performances of these NRs in the photodegradation of organic dyes (Fig. S4) showed a similar trend.

We performed control experiments to explore the synthetic mechanism, as shown in Fig. S1. High selectivity for the formation of PdS on the two ends of CdSe@CdS NRs can be achieved by increasing the temperature and the concentrations of the Pd and S precursors. According to previous reports, PdS

Fig. 2. UV-Vis absorption spectra (a) of CdSe@CdS nanorods (1), Au-CdSe@CdS nanorods (2), and PdS-CdSe@CdS-Au nanorods (3); PL spectra (b) of CdSe@CdS nanorods (1) and PdS-CdSe@CdS-Au nanorods (2), showing strong fluorescence quenching by PdS and Au due to rapid charge separation.

Fig. 3. Photocatalytic activity (a) of CdSe/CdS nanorods (1), Au-CdSe/CdS nanorods (2), and PdS-CdSe/CdS-Au nanorods (3). Photo-erosion tests comparison between CdSe/CdS nanorods (b) and PdS-CdSe/CdS-Au nanorods (c). CdSe/CdS nanorods were photo-irradiated under Xe light for 1.5 h while PdS-CdSe/CdS-Au nanorods were photo-irradiated under Xe light for 4 h.

formation mainly involves kinetically driven cation exchange [19]. We therefore hypothesized that cation exchange on one tip only is feasible. The kinetically controlled formation of CdSe/CdS NRs with Au on only one tip was reported earlier [18]. The reason for one-tipped NR formation is as follows. First, the chemical potential of a nanocrystal surface is inversely related to its radius (the Gibbs-Thomson effect). This suggests that secondary nucleation and growth should occur more rapidly on the tips than on the sides. Secondly, the atomic structure of cadmium chalcogenide NRs is not centrosymmetric; one tip is sulfur rich, resulting in preferential deposition of Au on that tip. We therefore tentatively propose that the mechanism of PdS-CdSe/CdS-Au NR formation is as follows. Au is deposited on the favored end, and this increases the chemical potential of that tip, preventing deposition of PdS on the same end. PdS is then deposited on the other end via partial cation exchange. On the basis of the H₂ production experimental results and literature reports, we propose the H₂ production mechanism shown in Fig. 4. The energy band gaps of CdS and PdS are 2.4 and 1.6 eV, respectively [6]. As discussed above, excited electrons from the CdS NRs are transferred to the Fermi level of Au and holes are transferred to PdS, because of band alignment. This greatly facilitates charge separation, and electron and hole transport to the opposite ends, greatly

reducing recombination rates. Protons are therefore efficiently reduced on CdS NRs and Au tips, and this significantly increases the H₂ production efficiency. We suggest that the large surface-to-volume ratio of the NRs and ease of access to reactants because of the small NR diameter also play a role.

In conclusion, we synthesized asymmetrically tipped PdS-CdSe/CdS-Au NR HCs by a wet-chemical method. Their UV-Vis absorption spectra showed strong electronic coupling between both tips, i.e., PdS and Au, and the CdS body, resulting in partial disappearance of the CdS absorption peaks. PdS-CdSe/CdS-Au NRs gave a H₂ production rate of ca. 1100 μmol over 5 h. This is two orders of magnitude greater than the rate achieved using Au-CdSe/CdS NRs, with only one tip. PdS-CdSe/CdS-Au withstood 4 h of photoirradiation, compared with 1.5 h for CdSe/CdS NRs, indicating that the photostability of PdS-CdSe/CdS-Au NRs is better than that of CdS. The experimental results and control experiments indicated that the improved photocatalytic activity and stability are the result of efficient charge separation and rapid transport in asymmetrically tipped linear PdS-CdSe/CdS-Au HCs.

References

- [1] Y. Y. Zhu, Y. J. Wang, Q. Ling, Y. F. Zhu, *Appl. Catal. B*, **2017**, 200, 222–229.
- [2] S. S. Chen, Y. Qi, Q. Ding, Z. Li, J. Y. Cui, F. X. Zhang, C. Li, *J. Catal.*, **2016**, 339, 77–83.
- [3] H. L. Wang, L. S. Zhang, Z. G. Chen, J. Q. Hu, S. J. Li, Z. H. Wang, J. S. Liu, X. C. Wang, *Chem. Soc. Rev.*, **2014**, 43, 5234–5244.
- [4] H. J. Yan, J. H. Yang, G. J. Ma, G. P. Wu, X. Zong, Z. B. Lei, J. Shi, C. Li, *J. Catal.*, **2009**, 266, 165–168.
- [5] J. H. Yang, H. J. Yan, X. L. Wang, F. Y. Wen, Z. J. Wang, D. Y. Fan, J. J. Shi, C. Li, *J. Catal.*, **2009**, 290, 151–157.
- [6] Q. Z. Wang, J. J. Li, N. An, Y. Bai, X. L. Lu, J. Li, H. C. Ma, R. F. Wang, F. P. Wang, Z. Q. Lei, W. F. Shangguan, *Int. J. Hydrogen Energy*, **2013**, 38, 10761–10767.
- [7] M. Schreier, J. S. Luo, P. Gao, T. Moehl, M. T. Mayer, M. Grätzel, *J. Am. Chem. Soc.*, **2016**, 138, 1938–1946.
- [8] Y. Q. Qu, X. F. Duan, *Chem. Soc. Rev.*, **2013**, 42, 2568–2580.
- [9] C. C. Chen, J. J. Lin, *Adv. Mater.*, **2001**, 13, 136–139.
- [10] C. Z. Wang, L. Z. Fan, Z. H. Wang, H. B. Liu, Y. L. Li, S. H. Yang, Y. L. Li, *Adv. Mater.*, **2007**, 19, 3677–3681.
- [11] N. Z. Bao, L. M. Shen, T. Takata, D. L. Lu, K. Domen, *Chem. Lett.*,

Fig. 4. Proposed photocatalytic mechanism of PdS-CdSe/CdS-Au nanorods for H₂ production in water splitting.

Graphical Abstract

Chin. J. Catal., 2018, 39: 407–412 doi: 10.1016/S1872-2067(17)62970-X

Synthesis of PdS-CdSe@CdS-Au nanorods with asymmetric tips with improved H₂ production efficiency in water splitting and increased photostability

Xianmei Xiang, Lingjun Chou, Xinheng Li *

Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences

Asymmetrically tipped PdS-CdSe@CdS-Au nanorod heterostructures were successfully synthesized. The heterostructures greatly improved the photocatalytic activity and stability in H₂ production as a result of efficient charge separation.

2006, 35, 318–319.

[12] A. Kudo, Y. Miseki, *Chem. Soc. Rev.*, **2009**, 38, 253–278.[13] Y. Hu, X. H. Gao, L. Yu, Y. R. Wang, J. Q. Ning, S. J. Xu, X. W. Lou, *Angew. Chem. Int. Ed.*, **2013**, 52, 5636–5639.[14] S. Kudera, L. Carbone, M. F. Casula, R. Cingolani, A. Falqui, E. Snoeck, W. J. Parak, L. Manna, *Nano Lett.*, **2005**, 5, 445–449.[15] W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, *Science*, **2002**, 295, 2425–2427.[16] X. H. Li, J. Lian, M. Lin, Y. T. Chan, *J. Am. Chem. Soc.*, **2011**, 133, 672–675.[17] X. M. Xiang, L. J. Chou, X. H. Li, *Phys. Chem. Chem. Phys.*, **2013**, 15, 19545–19549.[18] S. Chakraborty, J. A. Yang, Y. M. Tan, N. Mishra, Y. T. Chan, *Angew. Chem. Int. Ed.*, **2010**, 49, 2888–2892.[19] Y. Shemesh, J. E. MacDonald, G. Menagen, U. Banin, *Angew. Chem. Int. Ed.*, **2011**, 50, 1185–1189.**不对称沉积合成PdS-CdSe@CdS-Au一维纳米异质结构及其光解水制氢性能**

向贤梅, 丑凌军, 李鑫恒*

中国科学院兰州化学物理研究所羰基合成与选择氧化国家重点实验室, 苏州研究院, 江苏苏州215123

摘要: 提高光催化剂在光照射下产生的电子/空穴分离效率是一个关键的科学问题之一,目前也是一个很大的挑战。最近,在纳米尺度,通过材料设计,在窄带半导体上沉积助催化剂(比如引进双助催化剂)形成异质结构,能够建立内建电场,从而使电子和空穴快速分离和传输,显示出很好的可见光量子效率。对于异质结构,纳米结构半导体如硫化镉具有表面积大、规整形貌、电子和空穴迁移路径短等优势。用纳米半导体硫化镉制备异质结构光催化剂已有很多报道,大多数研究集中于单一助催化剂来提高光催化活性,对于纳米结构的设计制备研究较少;对于稳定性研究,侧重于利用超薄碳膜包敷策略来提高光催化的稳定性。因此,复杂纳米异质结构的精准合成和稳定性仍是个不小的挑战。我们研究组发展了一种催化剂制备方法,可选择性地将Au纳米颗粒和PdS纳米颗粒分别沉积于一维硫化镉纳米棒的两端,并将所制备的催化剂应用于可见光光催化分解水制氢反应中。

本文报道了一种高选择性沉积助催化剂的新方法,制备了PdS-CdSe@CdS-Au一维纳米异质结构。首先用高温分解法和种子法制备了核壳结构的CdSe@CdS纳米棒,预先沉积纳米金在纳米棒的一端,然后PdS通过阳离子交换法高度选择性地沉积到纳米棒的另一端,形成火柴棒纳米结构。HRTEM结果显示Au和Pd分别高选择性地沉积在纳米棒的两端,助催化剂和纳米棒之间有一个清晰的界面,非外延生长。紫外-可见吸收光谱显示,Au和PdS与CdSe@CdS纳米棒之间有很强的电子耦合效应,相应的荧光光谱也显示,顶端的助催化剂使CdSe@CdS发生强的荧光淬灭效应。将PdS-CdSe@CdS-Au一维纳米异质结构用于光催化分解水制氢,发现5 h内产氢达到1100 μmol,是相应Au-CdSe@CdS催化剂产氢速率的2个数量级。同时考察了它的光催化稳定性,发现双助催化剂形成的火柴棒型纳米结构稳定性大大提高,经过4 h光照仍能保持很好的

形貌.

通过对照实验考察了PdS-CdSe@CdS-Au一维纳米异质结构的形成机理. 一端金纳米颗粒的形成主要是由于顶端曲率的Gibbs-Thompson效应和纳米棒顶端组成分布不对称的缘故, 而PdS的顶端高选择性沉积是在阳离子交换过程中两端化学性质发生变化等原因造成的. 最后提出了光催化性能提高机理, 主要是由于电子和空穴在一维纳米棒上快速向相反方向分离和传输, 既大大提高了光催化制氢效率, 也大大提高了光催化稳定性.

关键词: 光催化; 电荷分离; 助催化剂; 异质结构; 水分解

收稿日期: 2017-09-25. 接受日期: 2017-10-30. 出版日期: 2018-03-05.

*通讯联系人. 电话/传真: (0512)81880906; 电子信箱: xinhengli@licp.cas.cn

基金来源: 国家重点研发计划(2016YFE0105700); 国家自然科学基金(21573263); 江苏省自然科学基金(BK20151236).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).