Control of hole dynamics in CdS/ZnS core/mesoporous-shell nanorods for enhanced photocatalytic H_2 evolution under visible light

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Abstract: Photo-induced hole transfer is a key process to determine the performance of solar energy conversion and optoelectronic devices. However, exploring the hole dynamics in semiconductor nanoparticulate photocatalysts is still challenging. Herein, we succeeded in the observation of hole dynamics in the CdS/ZnS core/mesoporous-shell (CdS_{core}/ZnS_{shell}) nanorods (NRs) by using transient absorption spectroscopy. The CdS_{core}/ZnS_{shell} NRs exhibited high photocatalytic activity and excellent stability in H_2 evolution reaction under visible light irradiation due to efficient hole transfer and extraordinarily long-lived charge separation (> 2.4 ms).

Keywords: Hole transfer, Core/shell nanoparticle, Photocatalytic H_2 evolution.

1. Introduction

Photocatalytic water splitting for hydrogen evolution is one of the promising techniques for efficient solar energy conversion for solving the problems of energy crisis.[1-3] Among the sequential processes following the light harvesting, charge separation, and catalytic reaction, the vital issue for improving the performance in photocatalytic activities is the long-lived charge separation suppressing the unfavorable back reaction. Although the substantial efforts have been made to achieve a high efficiency of water splitting for H_2 evolution, the photo-induced hole transfer remains to be clarified. Recently, much attention has been paid to the Type-I CdS/ZnS system with high photocatalytic performance, in which unusual hole transfer from valence band of CdS to the ZnS is proposed.[4, 5] Efficient extraction of hole could inhibit the photo-corrosion to improve the performance in photocatalytic activities.[4] However, there have been no reports to clarify the hole-related phenomenon in the CdS/ZnS system. Recently, we have discovered that the triphenylamine derivative (TPA) is a good indicator for hole transfer because its cation radials ($TPA^{\cdot+}$) have specific absorption at around 780 nm.[6] Herein, we provided definitive experiments to investigate the dynamics of photocarriers and observation of the interfacial hole transfer in the CdS/ZnS core/mesoporous-shell (CdS_{core}/ZnS_{shell}) nanocrystals (NRs) for the first time. The CdS_{core}/ZnS_{shell} NRs exhibited high H_2 evolution efficiency due to the efficient hole transfer and exceptionally long-lived charge separation. The combination of hole indicator and transient absorption spectroscopy shed light on the hole dynamics in the CdS_{core}/ZnS_{shell} NRs.

2. Experimental

The CdS_{core}/ZnS_{shell} NRs were synthesized by a seeded growth method. The detailed experiments are as follows: A mixture of Zn acetate (1 mmol), oleic acid (2 mL), and 1-octadecene (6 mL) was degassed at 150 °C for 30 min, heated at 250 °C for 1 h under a nitrogen atmosphere, and cooled to 70 °C. Then, the CdS NRs hexane solution (0.05 M, 2 mL) was swiftly injected to this solution. The mixture was degassed for 30 min under vacuum, and the reaction temperature was raised to 250 °C. The mixture of S (0.5 mmol) and trioctylphosphine (2 mL) was added to the above solution at the rate of 0.1 mL/min. At 40 min after the injection process, the solution was cooled to room temperature, washed three time by chloroform–ethanol mixed solution, centrifuged, and dispersed in the chloroform for further characterizations.

3. Results and discussion

Figure 1a shows a representative TEM image of the CdS_{core}/ZnS_{shell} NRs. The ZnS_{shell} surrounding the CdS NCs is clearly observed. As shown in the diagram of energy level of CdS_{core}/ZnS_{shell} NRs, the band alignment provides the suitable driving force to achieve the hole transfer. As shown in Fig. 1b, the CdS_{core}/ZnS_{shell} NRs exhibited high photocatalytic H_2 evolution and excellent stability maintaining 83%

activity after 72 h under visible light irradiation. By using the TPA-SH as an indicator of hole transfer, the dynamics of hole transfer from CdS phase to ZnS phase in CdS_{core}/ZnS_{shell} NRs were revealed by transient absorption spectroscopy. The ultralong-lived charge separation (> 2.4 ms) in CdS_{core}/ZnS_{shell} NRs could be a reason for the efficient photocatalytic activities. We consider that both the efficient hole extraction inhibiting the photo-corrosion and extraordinarily long-lived charge separation in CdS_{core}/ZnS_{shell} NRs achieve the good performance of photocatalyst.

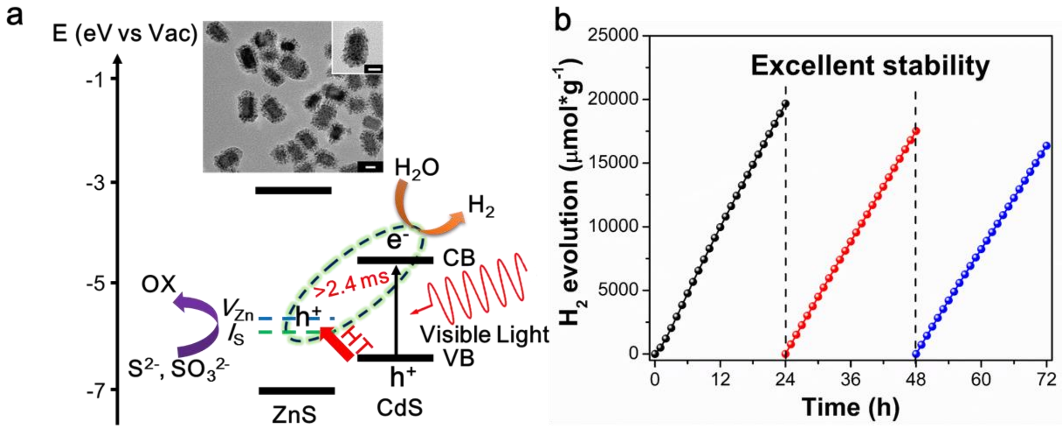

Figure 1. (a) Schematic energy level diagram of CdS NRs and ZnS NCs and the proposed mechanism of hole transfer and long-lived change separated state for enhanced photocatalytic H_2 evolution. Inset: typical TEM image of the CdS_{core}/ZnS_{shell} NRs, scale bar: 20 nm. (b) Recycling testing of the CdS_{core}/ZnS_{shell} NRs under visible light irradiation ($\lambda > 422$ nm) using the Na_2S–Na_2SO_3 aqueous solution as hole scavengers.

4. Conclusions

We provided definitive experimental evidence to elucidate the kinetics of visible-light-induced hole transfer at the CdS/ZnS heterointerfaces. The CdS_{core}/ZnS_{shell} NRs exhibited a visible-light-driven efficient and stable photocatalytic H_2 evolution reaction (apparent quantum yield: 12% at 400 nm and excellent stability maintaining 83% activity after 72 h). Interestingly, extraordinarily long-lived (> 2.4 ms) charge separation of photo-induced carriers was revealed by transient absorption spectroscopy. Furthermore, the trace of hole transfer in a CdS_{core}/ZnS_{shell} NR by using 4-diphenylaminobenzenethiol (TPA-SH) clarified the hole dynamics at the CdS/ZnS heterointerface. The present results pave the way for the fundamental research of the photo-induced carrier dynamics at nanoscale heterointerfaces and the improvement of efficient solar energy conversion.

References

1. Q. Wang, T. Hisatomi, Q. Jia, H. Tokudome, M. Zhong, C. Wang, Z. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. Li, I.D. Sharp, A. Kudo, T. Yamada, K. Domen, Nat. Mater. 15 (2016) 611-615.
2. Z. Lian, P. Xu, W. Wang, D. Zhang, S. Xiao, X. Li, G. Li, ACS Appl. Mater. Interfaces 7 (2015) 4533-4540.
3. Z. Lian, W. Wang, G. Li, F. Tian, K.S. Schanze, H. Li, ACS Appl. Mater. Interfaces 9 (2017) 16959-16966.
4. Y.P. Xie, Z.B. Yu, G. Liu, X.L. Ma, H.-M. Cheng, Energy Environ. Sci. 7 (2014) 1895-1901.
5. D. Jiang, Z. Sun, H. Jia, D. Lu, P. Du, J. Mater. Chem. A 4 (2016) 675-683.
6. K. Hu, A.D. Blair, E.J. Piechota, P.A. Schauer, R.N. Sampaio, F.G.L. Parlane, G.J. Meyer, C.P. Berlinguette, Nat. Chem. 8 (2016) 853-859.