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Highlight

A new heterojunction in photocatalysis: S-scheme heterojunction

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To harness abundant and clean solar energy along with relieving energy and environmental issues, photocatalysis holds great promise. Semiconductor-based photocatalysts are crucial to its successful application. However, the photocatalytic efficiency based on a unitary semiconductor material falls short of expectations, mainly because of the rapid recombination of photogenerated electrons and holes. This originates in the extremely strong Coulombic force between them. Moreover, it is impossible for a single photocatalyst to achieve wide light absorption and ample redox ability concurrently.

To tackle with this, heterojunction construction is highly desirable, which can not only solve the aforementioned problems, but also decouple oxidation and reduction reactions. Recently, a novel S-scheme heterojunction has been proposed and discussed by Prof. Yu's group in Wuhan University of Technology [1]. They gave a thorough summary on the necessity of raising such a new heterojunction. Besides, they analyze the deficiencies of the currently prevailing heterojunctions, especially the inherent fault of charge transfer. To date, two kinds of heterojunctions are extensively explored. One is type-II heterojunction composed of photocatalyst I (PC I) and PC II, and the other is Z-scheme heterojunction. As for the former, as shown in Fig. 1(A), it is believed that photogenerated electrons flow from the conduction band (CB) of PC I to that of PC II; while photogenerated holes migrate from the valence band (VB) from PC II to PC I. Although the as-claimed charge transport has been accepted for years, it is confronted with some problems after Prof. Yu's group mulled it over. Dynamically, it is difficult to realize the continuous charge transfer in type-II mode due to three reasons (as illustrated in Fig. 1(B)): (1) Repulsion between electrons in PC II and those transferred from PC I due to strong Coulombic repulsion force; (2) Repulsion between holes in PC I and those transferred from PC II; (3) Attraction between the holes/electrons in PC I and PC II. Thermodynamically, this charge separation sacrifices the original redox abilities of these two photocatalysts.

Another big family of heterojunction is Z-scheme heterojunction, which emerges to imitate natural photosynthesis. This family is composed of traditional [2], all-solid-state [3] and direct Z-scheme [4] heterojunctions. Similarly, the declared

charge transfer in the former two heterojunctions is also problematic. Considering the traditional Z-scheme, which makes use of the shuttle redox ion pairs, the as-proposed charge transfer route (Fig. 2(A)) is not workable. Thermodynamically, the electron pathway from CB of PC I to the acceptor (A) is more favored than that from CB of PC II to A, mainly due to the larger redox potential difference. Analogously, holes from PC II instead of those from PC I prefer to be captured by the donor (D), owing to the same reason. Ultimately, in this case, the so-called traditional Z-scheme fails to achieve maximized oxidation and reduction abilities. Namely, the holes stay at the VB of PC I instead of PC II, and electrons reside at CB of PC II instead of PC I, as shown in Fig. 2(B).

In the case of all-solid-state Z-scheme, which replaces the redox shuttle with conductive metals or carbon, it extends the application scope of its traditional counterpart. Nevertheless, the asserted charge transfer resists a closer examination from the following aspects. (1) Schottky barriers will form at the interface between PC I or PC II and the conductor after equalizing their Fermi levels, which prevents the continuous electron transfer [1]. (2) The charge transfer problems faced by its traditional Z-scheme counterpart are still unresolved. Some conceptual issues exist in the suggested charge transfer, as illustrated in Fig. 2(C). Specifically, the conductor plays the same role as the redox shuttles in traditional Z-scheme. Electrons at the CB of PC I own higher potential than those at the CB of PC II, which are much easier to migrate to the conductor, rather than the other way around. This is also applicable to the holes of PC II, which are highly likely to transfer to the conductor because of the stronger driving force. Eventually, the electrons from PC I meet the holes from PC II at the conductor, and they are annihilated. Meanwhile, electrons at the CB of PC II and holes at the VB of PC I are reserved (Fig. 2(D)). When viewed as a whole, no significant enhancement in the overall redox abilities can be realized by these three types of heterojunctions, i.e. type-II, traditional Z-scheme and all-solid Z-scheme. Three of them are subject to an identical drawback: that is, electrons and holes with inferior redox abilities participate in the corresponding photocatalytic reactions.

Direct Z-scheme heterojunction [4,5] develop from its for-

Fig. 1. Charge-transfer route in type-II heterojunction and its inadequacies. (A) type-II heterojunction. (B) like charges repel and opposite charges attract due to coulombic force. PC I and PC II stand for photocatalyst I and photocatalyst II, respectively. Figures taken from Ref. [1].

mer two generations, i.e. traditional and all-solid-state heterojunctions. Therefore, it is susceptible to be misunderstood because of the problems of the former two generations.

Against this backdrop, a new heterojunction concept (namely, S-scheme heterojunction) was proposed by Yu and his co-workers. By inductive thought, they initiated the classification of photocatalysts into oxidation photocatalysts (OP) and reduction photocatalysts (RP). OP, whose VB positions are relatively low, are mainly used in environmental degradation. In OP, photogenerated holes are useful and the corresponding electrons need to be quenched efficiently by oxygen. Similarly, RP, with a high CB, finds application in solar fuel production (H₂ production and CO₂ reduction). And normally the useless holes should be swiftly removed by sacrificial agents to avoid carrier recombination. An S-scheme heterojunction is constituted by RP and OP with staggered band structures, which is similar to the construction of type-II heterojunction, but their charge transfer are entirely different (Figs. 1 and 3). In S-scheme heterojunction, the powerful photogenerated electrons and holes are reserved in the CB of RP and VB of OP, respectively, while the pointless photogenerated charge carriers are recombined (Fig. 3(C)). There are three factors enhancing the transfer and separation of photogenerated electrons and holes in S-scheme heterojunction, internal electric field, band bending and Coulombic attraction between electrons and holes. Overall, compared with type-II and Z-scheme heterojunctions, S-scheme heterojunction possess reasonable charge-transfer route as

Fig. 3. Charge-transfer processes in an S-scheme heterojunction before contact (A), after contact (B), and photogenerated charge carrier transfer process under light irradiation (C). Figures taken from Ref. [1].

well as vivid designation.

Furthermore, S-scheme photocatalysts have demonstrated their potential in various fields, not confined to hydrogen evolution [6,7], CO₂ reduction [8], pollutant degradation [9] and even bacteria disinfection [10]. Yu and his colleagues believe that they are also feasible in other areas. Three types of characterization for S-scheme heterojunction are concluded: Ex-situ/in-situ light irradiation X-ray photoelectron spectroscopy, electron paramagnetic resonance and Atomic force microscopy.

To recapitulate briefly, this pioneering perspective established a promising heterojunction. Fresh concepts along with vast outlook are key indication of its value. Collective efforts will be spent on the development of other S-scheme heterojunctions for photocatalysis, and related charge carrier transfer and reaction mechanism.

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References

- [1] Q. Xu, L. Zhang, B. Cheng, J. Fan, J. Yu, *Chem*, **2020**, 6, 1543–1559.
- [2] A. J. Bard, *J. Photochem.*, **1979**, 10, 59–75.
- [3] H. Tada, T. Mitsui, T. Kiyonaga, T. Akita, K. Tanaka, *Nat. Mater.*,

Fig. 2. Problems faced by charge transfer route in traditional and all-solid-state Z-scheme heterojunctions. (A) original proposed and (B) thermodynamically favored charge-transfer mode in traditional Z-scheme photocatalysts. (C) original proposed and (D) thermodynamically favored charge-transfer mode in all-solid-state Z-scheme photocatalysts. Figures taken from Ref. [1].

Graphical Abstract

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The conceptual innovation, origin, progress, state-of-the-art developments, importance and challenges of S-scheme heterojunctions are briefly discussed in this highlight. It is expected to achieve the precise design and extensive applications of new S-scheme heterojunction photocatalysts.

2006, 5, 782–786.

[4] M. Gratzel, *Nature*, **2001**, 414, 338–344.[5] X. Wang, G. Liu, Z. G. Chen, F. Li, L. Wang, G. Q. Lu, H. M. Cheng, *Chem. Commun.*, **2009**, 3452–3454.[6] J. Fu, Q. Xu, J. Low, C. Jiang, J. Yu, *Appl. Catal. B*, **2019**, 243, 556–565.[7] D. Ren, W. Zhang, Y. Ding, R. Shen, Z. Jiang, X. Lu, X. Li, *Solar RRL*,

2020, 4, 1900423.

[8] Z. Wang, Y. Chen, L. Zhang, B. Cheng, J. Yu, J. Fan, *J. Mater. Sci. Technol.*, **2020**, <https://doi.org/10.1016/j.jmst.2020.02.062>.[9] J. Wang, Q. Zhang, F. Deng, X. Luo, D.D. Dionysiou, *Chem. Eng. J.*, **2020**, 379, 122264.[10] P. Xia, S. Cao, B. Zhu, M. Liu, M. Shi, J. Yu, Y. Zhang, *Angew. Chem. Int. Ed.*, **2020**, 59, 5218–5225.

新型光催化异质结: S型异质结

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摘要: 太阳能是最丰富的清洁和可再生能源, 光催化技术在太阳能利用中具有很大潜力, 这有赖于高效半导体光催化剂的设计制备。然而, 单一光催化剂效率很低, 主要是光生电子和空穴的强库伦吸引力导致它们快速复合。此外, 单一光催化剂也很难同时具有宽光谱吸收和足够的氧化还原能力。为了解决这一问题, 构建异质结光催化剂成为一种有效途径, 因为它可以实现光生电子和空穴在空间上的有效分离。针对传统的II型和Z型异质结在动力学和热力学方面的缺陷, 2019年由武汉理工大学余家国教授团队提出梯形异质这一新型异质结概念。对于II型异质结, 热力学和动力学分析表明光生载流子的转移机理不正确。热力学和动力学分析表明光生载流子的转移机理不正确。而Z型异质结系统主要包括传统、全固态和直接Z型异质结三种类型。对于前两种异质结, 它们的界面电子转移存在理论问题。传统Z型异质结利用氧化还原电对, 而电子受体和给体更容易从与其具有较大的电势差的半导体接受或给予电子。全固态Z型异质结利用导体, 比如导电金属或碳材料, 取代氧化还原电对, 从而使其应用范围由液态扩展到固态。然而通过进一步分析, 它的电荷传输也有漏洞。首先, 界面的肖特基势垒抑制电荷持续传输, 此外, 全固态Z型异质结中的导体与传统Z型中氧化还原电对的作用如出一辙。因此, 传统Z型的问题在这里也依旧存在。总的来说, II型、传统和全固态Z型都面临相同的问题, 就是光生电子和空穴拥有较弱的还原和氧化能力, 而S型异质结则与它们截然不同。该异质结由氧化型和还原型光催化剂组成, 内建电场、能带弯曲和库仑力三大作用促使氧化型的光生电子与还原型的光生空穴复合, 同时阻止氧化型的光生空穴与还原型的光生电子转移。最终, 电子和空穴分别具有高的还原和氧化能力。由于其优越性, S型异质结在各种光催化应用中引起了广泛的兴趣, 包括产氢、二氧化碳还原、污染物降解和灭菌等领域。而S型异质结机理可以用X射线光电子能谱、电子顺磁共振和原子力显微镜进行表征。S型异质结崭露头角, 未来发展可期。

关键词: S型异质结; 异质结光催化剂; 电荷分离机制; 充电转移路线; Z型光催化剂

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