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Communication

Photo-induced self-formation of dual-cocatalysts on semiconductor surface

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ABSTRACT

Cocatalyst plays key roles in photogenerated charge separation and surface catalytic reactions in photocatalysis. However, it is not clear if the chemical states of cocatalysts changed or remains unchanged under photocatalytic reaction conditions. Herein, taking NaTaO₃ as an example, we systematically investigated the chemical states of nickel-based cocatalysts during photocatalytic water splitting reaction. It was found that photo-induced self-formation of Ni and NiO cocatalyst species take place on the surface of NaTaO₃ nanocrystals. The self-formation of dual-cocatalysts not only occurs on 26-facet NaTaO₃, but also takes place on a more general 6-facet NaTaO₃. Our work clarified that the chemical states of cocatalysts are changing and the redox dual-cocatalysts are redistributed on the semiconductor surface owing to the reaction induced by photogenerated charges under the condition of photocatalytic reactions.

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Photogenerated charge separation and surface catalytic reactions are prerequisites for photocatalysis, in particular for photocatalytic overall water splitting [1–8]. Proper cocatalysts can serve as active sites for surface reactions and improve charge separation and charge utilization [9,10]. An interesting issue concerning cocatalysts is the chemical state of cocatalysts, which is not clear for most of the photocatalysts under working conditions. Notably that photo-generated electrons and holes transfer to the cocatalysts for chemical reactions, therefore, it is inevitable that the chemical states of the cocatalyst are changed under photocatalytic reactions. However, how the redox cocatalyst evolves under photocatalytic reaction has long been not clear.

Nickel or nickel oxide are considered as the efficient cocatalysts for photocatalytic water splitting on semiconductor-based photocatalysts [11]. It was found that the nickel-based cocatalyst in K₄Nb₆O₁₇ photocatalyst was required to be pretreated by H₂ and then oxidized by O₂, possibly forming a Ni/NiO core/shell structured cocatalyst, which was beneficial for photocatalytic water splitting [12]. Townsend et al. [13] suggested that nickel-based cocatalyst on SrTiO₃ is more likely a three components Ni-SrTiO₃-NiO with Ni as reduction cocatalyst and NiO as oxidation cocatalyst. Han et al. [14] recently reported that co-catalysts showed a variation from Ni@NiO_x core-shell to Ni and NiOOH species, which served as reduction and oxidation cocatalysts on SrTiO₃-based photocatalyst, respectively.

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Zhang et al. [15] found more than one nickel species on equivalent facet of NaTaO₃ nanocrystals. These reports on the nickel-based cocatalysts in water reduction and/or oxidation reactions were often contradictory in the literature, which is largely due to the difficulty to distinguish the exact chemical states and the surface distribution of cocatalysts under photocatalytic reactions.

Separation of dual-cocatalysts on different facets has recently been demonstrated to be an effective strategy for suppressing reverse reaction and enhancing charge separation in photocatalysis [16–20]. In this work, taking nickel deposited NaTaO₃ as an example, we investigate the chemical states of nickel-based cocatalysts derived during photocatalytic water splitting reaction. An interesting photo-induced self-formation of Ni and NiO cocatalysts was found on the surface of NaTaO₃ nanocrystals. The self-formation of redox dual-cocatalysts are spatially separated on the surface of NaTaO₃ nanocrystals.

Two types of NaTaO₃ nanocrystals were synthesized with anisotropic facets (26-facet NaTaO₃) and isotropic facets (6-facet NaTaO₃) [21]. Photodeposition method can be used to determine the distribution of photogenerated electrons and holes [22]. For 26-facet NaTaO₃ (Fig. 1), most Pt particles were selectively deposited on {001} facets while majority Co₃O₄ particles only appeared on {011} and {111} facets, suggesting that photogenerated electrons and holes can be spatially separated between different facets of NaTaO₃ nanocrystals. It shows that both Pt and Co₃O₄ particles are all randomly deposited on all the facets of 6-facet NaTaO₃ (Fig. S1), indicating that the photogenerated electrons and holes are randomly distributed on every facet. The two types of nanocrystals possess similar crystalline structures (Fig. S2), light absorption properties (Fig. S3) and surface areas etc. (Table S1). Therefore, it is feasible to investigate the chemical states of nickel-based cocatalysts according to the spatial charge separation. Fig. 1(c) shows the shape-controlled growth of 26-facet NaTaO₃ nanocrystals, with smooth facet and regular morphology, exposed with {001}, {011} and {111} facets. Fig. 1(d) and Fig. S1(c) show 26-facet NaTaO₃ and 6-facet NaTaO₃ schematically. EDS of Pt or Co₃O₄

deposited on 26-facet NaTaO₃ are shown in Fig. S4, but part of the element Pt signal was obscured by the signal of element Ta. Therefore, XPS of Pt or Co₃O₄ deposited on 26-facet NaTaO₃ are shown in Fig. S5. Pt 4f in XPS revealed that the deposited element was in the metallic form. According to the binding energy of Co 2p in XPS, the specie can be ascribed to Co₃O₄. The influence of different facet structure was verified by a traditional impregnation method. This method is based on the surface structure and adsorption factor. The nanoparticles are distributed on all the facets of 26-facet NaTaO₃ randomly by impregnation method (Fig. S6). However, in photodeposition method, two different nanoparticles are distributed on the surface of 26-facet NaTaO₃ spatially. Therefore, this impregnation method has relatively weak influence by different facet structures when compared with photodeposition method.

As an efficient cocatalyst, nickel oxide was used to load on the surface of NaTaO₃ nanocrystals by conventional impregnation method, usually this method can make the cocatalysts distribute uniformly on all the facets of nanocrystals [23–31]. EDS of cocatalysts deposited 26-facet NaTaO₃ are shown in Fig. S7. But EDS cannot characterize the chemical state of nickel species, just the element nickel. Therefore, the cocatalyst was characterized by XPS before and after photo irradiation on 26-facet NaTaO₃ nanocrystals further. The impregnated sample is confirmed by XPS and the result gives only the peak of NiO species (2p_{3/2} at 854.9 eV) before photo illumination (Fig. 2(a)). After photo illumination with water under the protection of argon (to isolate the O₂ in the air, in case the metallic Ni was oxidized by O₂), the XPS peak of metallic Ni (2p_{3/2} at 852.9 eV) was observed. It is clear that both Ni and NiO present distinct peaks in XPS after illumination, indicating that at least part of NiO loaded by impregnation method can be reduced to metallic Ni by the photogenerated electrons during the illumination process (Fig. S8).

The impregnated NiO was also fully reduced by H₂. Only the XPS of metallic Ni can be observed (Fig. 2(b)), suggesting that NiO was reduced to element Ni. After photo illumination with water under the protection of argon, the XPS peak of NiO appears with the coexisting of metallic Ni. It is clear that both Ni and NiO species are produced, demonstrating that part of metallic Ni has been oxidized by the photogenerated holes during the illumination process.

Fig. 3 shows the TEM images of cocatalysts species on different facets of 26-facet NaTaO₃ with depositing NiO by impregnation method. NiO deposited by impregnation method were small particles (Fig. 3(a)). After photo illumination, most particles on {001} facets and the species on {011} facets manifest different morphologies between each other (Fig. 3(b)). More TEM image for cocatalysts on each facet is shown in Fig. S9. Fig. 3(c) shows that the lattices on {011} facet match well with NiO (the same position as an oxidation cocatalyst Co₃O₄ in Fig. 1(b); PDF#47-1049). Similarly, in Fig. 3(d), the lattice distance of Ni can be seen on {001} facet (the same position as reduction cocatalyst Pt in Fig. 1(a); PDF#45-1027). The separation of photogenerated electrons and holes makes the Ni and NiO dual-cocatalysts distributed on different facets. The changes of nickel species before and after photo illumination demon-

Fig. 1. Photo-reduction of Pt and photo-oxidation of Co₃O₄ on 26-facet NaTaO₃ nanocrystals. (a) Pt/26-facet NaTaO₃; (b) Co₃O₄/26-facet NaTaO₃; (c) Shape-controlled growth of 26-facet NaTaO₃ nanocrystals; (d) Schematic model of 26-facet NaTaO₃.

Fig. 2. XPS spectra of impregnated NiO (a) and reduced Ni (b) before and after illumination on 26-facet NaTaO₃.

strate the self-formation of Ni/NiO dual-cocatalysts on 26-facet NaTaO₃. After reactions reach to equilibrium, Ni and NiO can be located on different facets. The above results indicate an interesting phenomenon of self-formation of Ni and NiO cocatalysts by photogenerated charges when NaTaO₃ photocatalyst was excited under light irradiation.

This phenomenon can be also seen in the overall water splitting test for NaTaO₃-based photocatalysts with different cocatalysts deposited. NiO/NaTaO₃ was prepared by impregnation method and Ni/NaTaO₃ by impregnation method and followed by a reduction in H₂ atmosphere. For the impregnated NiO/NaTaO₃ photocatalyst (Fig. 4(a) and (c)), the ratio of H₂ to O₂ was slightly smaller than 2.0 at initial time of reaction, which means that some photogenerated electrons were consumed to

reduce NiO species to Ni. As the reaction time was prolonged, the ratio of H₂ to O₂ reached to a stoichiometric value gradually. These processes can be described as following equations:

On the contrary, for the fully reduced Ni photocatalysts (Fig. 4(b) and (d)), the initial ratio of H₂ to O₂ was a bit greater than 2.0 because part of the photogenerated holes were consumed for oxidizing the metallic Ni to NiO. The ratio of H₂ to O₂ was approaching to 2.0 as the oxidation of Ni to NiO reached to equilibrium. These processes can be described as following equations:

The final performances of two different photocatalysts are almost at the same level after photo illumination for a long time, due to the equilibrium between Ni and NiO.

Both HRTEM and photocatalytic water splitting results evidence a self-formation phenomenon of Ni and NiO species on 26-facet NaTaO₃ photocatalyst under the light irradiation, which was also demonstrated by XPS characterization. On 6-facet NaTaO₃ nanocrystals with isotropic facets exposed (Fig. 5(a)), HRTEM images show different morphologies of the nickel species after photo illumination. Similar to the cocatalysts on 26-facet NaTaO₃, it can be found that different morphologies of cocatalysts appear on the surface of 6-facet NaTaO₃ (Fig. 5(b)). More TEM image can be seen in Fig. S10. The lattices of the selected area in Fig. 5(b) match well with the metallic nickel and nickel oxide, respectively (Fig. 5(c)). Therefore, the self-formation of dual-cocatalysts can also occur on a more general 6-facet NaTaO₃ nanocrystal with isotropic facet exposed by photogenerated electrons and holes. It should be noted that the widely-used NiO loaded NaTaO₃ photocatalysts gives high quantum efficiency in photocatalytic overall water splitting is possibly due to the generation of redox dual-cocatalysts for improving both reduction and oxidation surface reactions.

The overall water splitting activities on different Na-

Fig. 3. TEM images show morphologies change of nickel species as cocatalysts before (a) and after (b) photo-illumination on 26-facet NaTaO₃; (c) HRTEM images of nickel oxide as oxidation (a) and reduction (b) cocatalyst on {001} facet.

Fig. 4. Average photocatalytic overall water splitting activities of impregnated NiO (a) and reduced Ni (b) on 26-facet NaTaO₃. H₂/O₂ ratio of impregnated NiO (c) and reduced Ni (d) by the average photocatalytic overall water splitting performances on 26-facet NaTaO₃. Irradiated by Hg-Xe lamp.

Fig. 5. (a) Shape-controlled growth of 6-facet NaTaO₃ nanocrystals. (b) TEM image shows morphologies of nickel species after photo-illumination on isotropic facet of 6-facet NaTaO₃. (c) Amplification of the selected area in image (b) shows nickel oxide and metallic nickel on the surface of 6-facet NaTaO₃.

TaO₃-based photocatalysts are shown in Fig. S11. The enhancement of Ni/NiO deposited 26-facet NaTaO₃ can be attributed to the spatial charge separation between different facets. Scheme 1 describes the process of the whole charge separation on 26-facet NaTaO₃ and self-formation of dual-cocatalysts on 6-facet NaTaO₃. The energy diagram in Fig. S12 shows the functional role of Ni and NiO on NaTaO₃ semiconductor. The change of suspension pH value before and after photocatalysis is less than 0.2 and the leaching of element nickel (peak in UV-vis spectra at 395 nm) is too less to be detected in electrolyte after photo reaction. The reduction treatment of NiO at specific temperature won't destroy the surface structure of NaTaO₃ semiconductor (Fig. S13). Therefore, the above factors have less effect in this photocatalysis system. Photore-

duced metallic Ni was involved in the initial stage of photocatalytic overall water splitting, and the equilibrium between metallic nickel and nickel oxide as well as their location sites are crucial factors influencing the whole processes. At the beginning, NiO was impregnated uniformly on every facet. Subsequently, the photogenerated electrons reduce the nickel oxide to metallic state. This interesting phenomenon of self-formation for Ni and NiO cocatalysts by photogenerated charges not only takes place on 26-facet NaTaO₃, but also occurs on a more general 6-facet NaTaO₃.

In summary, taking nickel deposited NaTaO₃ as an example, we investigated the chemical state of nickel-based cocatalysts derived under working conditions. Interestingly, it was found that photo-induced self-formation of Ni and NiO cocatalyst spe-

Scheme 1. Schematic description of (a) spatial charge separation between different facets of 26-facet NaTaO_3 and (b) self-formation of Ni/NiO redox dual-cocatalysts on 6-facet NaTaO_3 by photogenerated charges.

cies on the surface of NaTaO_3 nanocrystals during photocatalytic water splitting reaction. The self-formation of dual-cocatalysts not only occurs on 26-facet NaTaO_3 , but also takes place on a more general 6-facet NaTaO_3 . These findings clarified the evolution of redox dual-cocatalysts during photocatalytic reaction in heterogeneous photocatalyst systems for solar energy conversion.

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Graphical Abstract

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Photo-induced self-formation of dual-cocatalysts on semiconductor surface

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Self-distribution of redox dual-cocatalysts on semiconductor surface can be achieved by photogenerated electrons and holes. This strategy promotes the photocatalytic activity to a high level, which will be benefit for solar energy conversion system.

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光诱导双助催化剂在半导体表面的自发形成

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摘要: 半导体光催化体系的助催化剂在光生电荷分离和表面催化反应过程中扮演着重要的角色。然而, 在反应条件下助催化剂的化学态是否发生改变尚不清楚。本文以钽酸钠为模型光催化剂, 系统地研究了镍基助催化剂在光催化分解水反应中的化学态。结果发现, 在光诱导条件下半导体钽酸钠单晶表面自发形成了金属镍和氧化镍双助催化剂。

首先用传统的水热法合成只暴露单一晶面的六面体钽酸钠半导体单晶光催化剂和暴露不等同晶面的二十六个面体钽酸钠半导体单晶光催化剂。原位光沉积结果显示, 暴露不同晶面的二十六个面体钽酸钠半导体单晶光催化剂存在晶面间的电荷分离现象, 进一步利用该现象可以确定不同催化活性位上镍基助催化剂的作用。XPS结果显示, 半导体钽酸钠单晶表面的镍基助催化剂存在的不同价态。高分辨透射电镜结果表明, 不同晶面上的镍基助催化剂具有不同的形貌, 并且通过晶格衍射条纹的对比确认了不同镍基助催化剂物种的归属和作用。

将表面浸渍氧化镍的二十六个面体钽酸钠半导体光催化剂用于全分解水测试发现, 反应开始阶段 $H_2:O_2$ 比值小于2:1, 说明部分光生电子被消耗掉, 用于还原氧化镍, 生成了金属镍。将表面还原的金属镍光催化剂进行全分解水测试发现, 反应开始阶段 $H_2:O_2$ 比值大于2:1, 说明部分光生空穴被消耗掉, 用于氧化金属镍, 生成了氧化镍, 金属镍和氧化镍最终在反应的过程中达到了平衡。金属镍负载在 {001} 晶面上, 起着还原助催化剂的作用, 参与质子还原, 释放出 H_2 ; 氧化镍负载在其他晶面上, 扮演着氧化助催化剂, 参与水的氧化, 释放出 O_2 ; 金属镍和氧化镍共同促进了光催化全分解水反应, 使反应活性达到了最高。这种双助催化剂的自发形成现象不仅存在于二十六个面体钽酸钠单晶半导体表面, 在六面体钽酸钠单晶半导体表面也同样存在, 是一个普适性的现象。在六面体钽酸钠半导体单晶光催化剂表面同样可以发现不同形貌的镍基助催化剂, 分别归属于金属镍和氧化镍。本文说明了助催化剂的化学态在光催化反应的条件下是可以发生改变的, 并且光生电荷可以在半导体表面诱导双助催化剂的自发形成。

关键词: 光催化; 助催化剂; 化学态; 光生电荷; 自发形成

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