Band Engineering of Tantalum Nitride Photocatalyst for One-Step Photoexcited Overall Water Splitting

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Abstract: Band structure of Ta_3N_5 semiconductor was tuned by the Mg+Zr substitution treatment. After loading with Ir/Cr_2O_3 cocatalyst and surface coating with an amorphous TiO_2 layer, the as-prepared series Ta_3N_5:Mg,Zr-based photocatalysts could realize one-step photoexcited overall water splitting (OWS) reaction. Detailed mechanism study showed that the proper band structure, effective cocatalyst and TiO_2 coating played a key role in achieving the OWS process.

Keywords: Band engineering, Photocatalysis, Tantalum nitride, Water splitting.

1. Introduction

Development of one-step photoexcited OWS photocatalysts with narrow band gap is of vital importance for the efficient solar light utilization. However, as the band gap of the semiconductor decreases, the driving force for the OWS reaction correspondingly decreases, making it difficult to use long wavelengths visible light. Ta_3N_5, as a typical 600-nm class semiconductor, has a thermodynamically matched band position for OWS reaction, but one-step photoexcited OWS process has never been achieved based on it. In order to check the possible reason of insufficient reaction driving force, Mg+Zr substitution treatment was applied here to tune the band structure of the modified Ta_3N_5[1]. Results showed that the absorption edges of the modified Ta_3N_5 samples could be continuously tuned from 600 to 555 nm. After deposition with core-shell structured Ir/Cr_2O_3 cocatalyst and surface wrapping with an amorphous TiO_2 layer[2,3], OWS reaction could proceed on the modified Ta_3N_5:Mg,Zr-based photocatalysts.

2. Experimental

The oxide precursors of Ta_2O_5:Mg,Zr with different molar ratios of Mg/Zr/Ta were prepared by a citric acid method[4]. For the nitridation process, the oxide precursor was heat-treated under 100 mL min^{-1} of dry NH_3 flow at 1173 K for 8 h. The nitrided powder was magnetically stirred for 3 days in ethanol, yielding well-dispersed particles. After dryness, Ir nanoparticles were deposited by impregnation and subsequently H_2 reduction treatment at 573 K for 1 h. Cr_2O_3 layer coated on the surface of Ir nanoparticles was realized by a photo-deposition method with K_2CrO_4 as the precursor, and an amorphous TiO_2 layer was deposited from a Ti-peroxide solution referred to the literature[2,3].

3. Results and discussion

XRD patterns showed that the as-prepared Ta_3N_5:Mg,Zr samples exhibited the main phase of Ta_3N_5. With increasing the introduced amounts of Mg and Zr elements, the diffraction peaks shifted to smaller angles due to the bigger ion radiuses of Mg^{2+} and Zr^{4+} than that of the Ta^{5+} ion. It needs to be noted that MgO is also detected on some heavily substituted samples[5]. Band absorption edges of the samples were decreased from 600 to 555 nm, as increasing the amount of foreign components. Here, the reduced tantalum species could be remarkably suppressed by this substitution method. SEM images showed that the particle size could also be significantly reduced for the modified samples.

Based on those developed Ta_3N_5:Mg,Zr samples, one-step photoexcited OWS process was tried with various modifications. Firstly, various core-shell structured cocatalysts were deposited on the surface of

Ta_3N_5:Mg,Zr sample. It was found that Ir/Cr_2O_3 was the best one and the Mg+Zr substitution could significantly improve the photocatalytic activities in pure water. However, oxygen evolution was hardly detected in those cases. In order to suppress the possible oxygen reduction reaction (ORR) and self-oxidation of oxynitride, an amorphous TiO_2 layer was further coated on the cocatalyst-modified photocatalysts. As shown in Fig. 1a, one-step photoexcited OWS process could be successfully achieved on the optimized photocatalysts. Possible reaction mechanism was thus proposed, which was shown in Fig. 1b. Here, the introduced Mg+Zr substitution can effectively modify the band structure of the Ta_3N_5, leading to a larger reaction driving force and efficient charge utilization. Further assisted with Ir/Cr_2O_3 co-catalyst and TiO_2 layer, some side reactions, such as ORR and hydrogen oxidation reaction, can thus be effectively inhibited. All of those aforementioned factors are highly important to realize the one-step photoexcited OWS process.

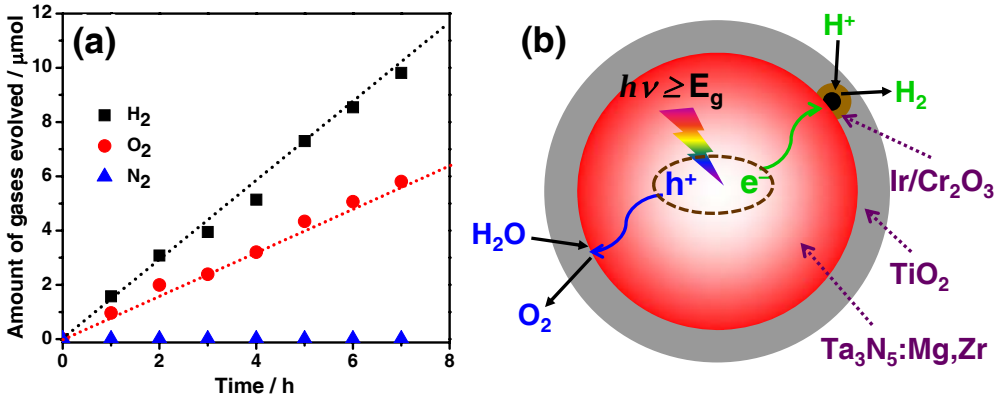

Figure 1. Photocatalytic OWS performance on the Ta_3N_5:Mg,Zr-based photocatalyst (a) and its possible schematic reaction mechanism (b). Reaction conditions: 0.15 g photocatalyst (2 *wt*% TiO_2-1 *wt*% Ir/3 *wt*% Cr_2O_3) with the Mg/Zr/Ta molar ratio of 1.5:0.5:8, 250 mL H_2O, 300 W Xe light, side irradiation type.

4. Conclusions

It was demonstrated that Mg+Zr substitution was an effective way to tune the band structure of the Ta_3N_5. Based on the as-developed Ta_3N_5 samples, one-step photoexcited OWS process could be achieved after surface modifications with Ir/Cr_2O_3 cocatalyst and TiO_2 layer. Although the obtained photocatalytic activity is low for the present case, it is one successful example of the one-step OWS based on the Ta_3N_5 semiconductor. The methods used here for the exploration of OWS process would be extensible to other (oxy)nitride-based photocatalysts with small band gap.

References

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