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Role of passivated N–F pairs in enhancing photoactivity of $ZnWO_4$ (010) surface: Emphasis on correlation between codoping forms and compensation mechanisms

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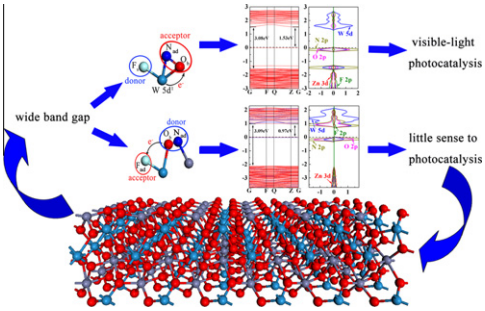
HIGHLIGHTS

- N–F codoping passivates the partially occupied states acted as trap of electrons.
- $N_{ad}F_s$ codoping achieves good visible-light photoactivity of $ZnWO_4$.
- $N_{ad}F_{ad}$-codoped $ZnWO_4$ (010) surface has little sense to photocatalytic process.

GRAPHICAL ABSTRACT

We reveal the correlation between codoping forms and compensation mechanisms in N–F pairs and their different effects on enhancing photoactivity of $ZnWO_4$ (010) surface.



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ABSTRACT

We perform first-principles density function theory calculations to study the correlation between codoping forms and compensation mechanism in N–F pairs at $ZnWO_4$ (010) surface. Our study considers substitutional as well as adsorptive and interstitial codoping forms at $ZnWO_4$ (010) surface, and the results show that all the N_sF_s, N_sF_{ad}, $N_{ad}F_s$, and $N_{ad}F_{ad}$ codoping forms can passivate the partially occupied states formed in the corresponding monodoped systems to enhance the photoactivity of $ZnWO_4$ (010) surface and decrease the transition energy of photoexcited electrons from the impurity levels to the conduction band minimum to low-energy area. There are four different compensation mechanisms in N–F pairs at $ZnWO_4$ (010) surface, corresponding to the four codoping forms, and different compensation mechanisms in N–F pairs result in different effects on photoactivity of $ZnWO_4$, such as the $N_{ad}F_{ad}$ has little sense to photocatalytic process, due to the electrons only transferring between the N_{ad}–O_b π^* states. We expected that this knowledge could introduce some more general useful codoping concepts to the design of visible-light photocatalysts.

1. Introduction

As is well known, the photocatalytic activity of most stable semiconductor photocatalysts is not high enough for their commercial applications due to their narrow light-response range and relatively easy recombination of photoexcited electron–hole pairs, such as titania (TiO_2), which has received intense attention as a promising photocatalytic material for years [1,2]. Though monodoping with metal or nonmetal elements is a promising approach to reduce the absorption threshold to visible region [3–13], photogenerated current of monodoping is low as shown in experimental studies [14,15], because the partially occupied impurity bands can act as recombination centers to increase the recombination rate of the charge carriers [16]. The cooperative

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