Improving photocatalytic activity of $K_2Ta_2O_6$ by Sulfur anion doping

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Abstract. The photocatalysts of S-doped $K_2Ta_2O_6$ have been successfully synthesized by hydrothermal method. Effects of S doping to the $K_2Ta_2O_6$ on the structure and photocatalytic performance are systematically investigated. The S was successfully introduced into the lattice sites of Ta^{5+} at the state of S^{6+}. The morphology was unchanged when the S was incorporated into the $K_2Ta_2O_6$. The band gap of $K_2Ta_2O_6$ was narrowed with the increase of S dopants. The photocatalytic test under UV-light irradiation indicated that the decomposing efficiency of MO and RhB was elevated with the incorporation of S. And the sample prepared from addition of 10% molar ratio of S precursor showed the highest photocatlytic performance.

Introduction

Tantalum-based photocatalysts have attracted the researchers' attention due to their unique structure and high performance for photocatalytic reaction, especially in the separation of water under irradiation of UV[1-2]. The photocatalytic performance of the $K_2Ta_2O_6$ with the pyrochlore-like structure was better than the the pervokites-like structure of $KTaO_3$ with the irradiation of UV, due to the $K_2Ta_2O_6$ has the distorted [TaO6] structure[3]. However, the pure $K_2Ta_2O_6$ presented low photocatalytic efficiency. Many methods are used to improve the photocatalytic activity of $K_2Ta_2O_6$, such as loading noble metal, metal doping, nonmetal incorporating. Xu[4] et al, prepared Ag-decorated $K_2Ta_2O_6$ nanocomposite photocatalysts, which enhanced visible light driven degradation activities of Tetracycline(TC). They found that the 3% molar ratio of Ag loading showed the highest decolorization efficiency. Zhu[5] et al, synthesized a novel $K_2Ta_2O_{6-x}N_x$ catalyst, which was from N-doped Ta_2O_5 precursors in KOH solution by a two-step hydrothermal process. And the activity of the samples decreased with the increase of N-doping concentration. $K_2Ta_2O_{5.982}N_{0.018}$ showed the highest photoactivity for the FAD degradation.

Based on previous work, we found that the nonmetal was always incorporated into Tantalate by the solid state reaction. And there were few reports about $K_2Ta_2O_6$ with S dopants. In this work, S-doped $K_2Ta_2O_6$ has been successfully prepared by hydrothermal method, which exhibited higher UV-light photocatalytic activity.

Experimental

Fabrication of S-doped $K_2Ta_2O_6$ all the reagents with analytical grade were used without further purification. In the typical process, 0.442g Ta_2O_5 was added into a Teflon-line stainless steel autoclave (30mL) capacity with 20mL 3M KOH. Then 0%, 5%, 10%, 15%, 20% molar ratio amount of $Na_2S_2O_3 \cdot 5H_2O$ were individually added into the solution. Then the autoclave was sealed and put into the oven at 200℃ for 12h after the mixture solution stirred 30min at room temperature. The precipitate was then filtered, repeatedly washed by water and ethanol and dried 4h at 90℃. The obtained samples from adding various S source content were marked as the x% S-KTO, where x is the molar ratio of $Na_2S_2O_3 \cdot 5H_2O$.

Characterization The crystal structure of obtained samples was characterized by Bruker/D8-advance with Cu Ka radiation (λ=1.518 Å) at the scanning rate of 0.2sec/step in the range of 5-80°. The surface morphology of samples was investigated by the Field-emission scanning electron microscope (FESEM, Hitachi S-4800) equipped with Energy- dispersive X-ray spectroscopy (EDS),

and transmission electron microscope (TEM, JEM2100, 200kV). MO and RhB were chosen as model pollutant for photocatalytic activity tests under UV-light (250W high mercury lamp). During the degradation experiments, 50mg catalyst were added into 100ml 15mg/L MO or $1*10^{-5}$M RhB. The mixture solution was stirred at dark for 30min before illumination. The photodegradation efficiency was monitored by measuring the change in intensity of the characteristic absorbance of MO, RhB at 464nm or 554nm, correspondingly, using Hitachi U-3900 at 10nm path length quartz cell.

Results and discussion

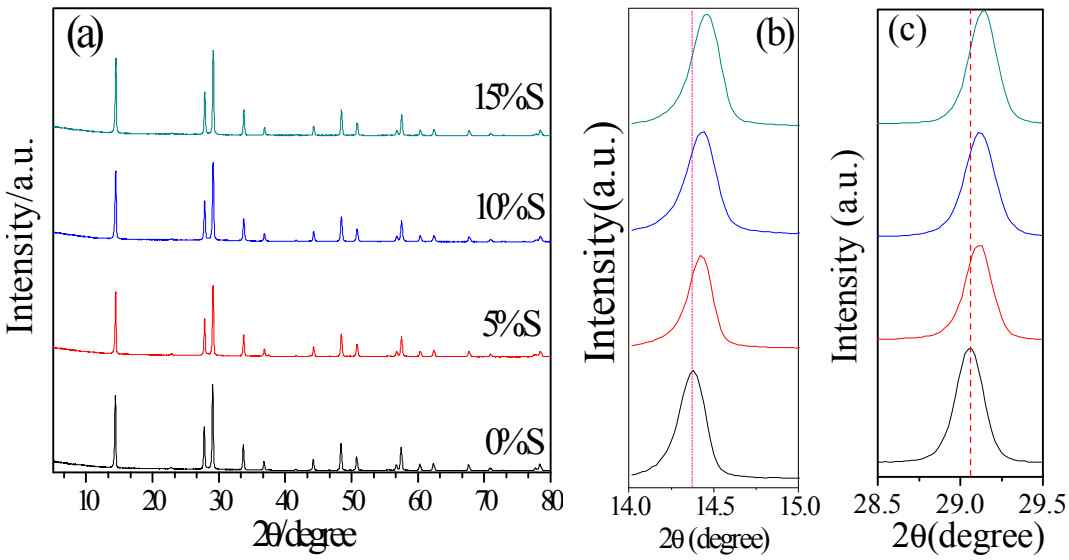

Fig1. (a)The XRD patterns of x%S-KTO(x=0, 5, 10 ,15), the magnified patterns of 2θ value in the 14-15°(b)and 28.5-29.5°(c).

The XRD patterns of x%S-KTO(x=0, 5, 10 ,15) with various doping amount are shown in Fig1. All the diffraction peaks of samples are closely correlate with the documented orthorhombic phase $K_2Ta_2O_6$ (PDF card number 35-1464). An interesting finding scrutinized from XRD patterns (Fig1.b and c) is that the (111) diffraction peaks in 14-15° and the (222) diffraction peaks in 28.5-29.5° shift into higher 2θ values with the increase of S sources from 5%mol to 15%mol, indicating that the lattice distance is decrease with the increase of S addition (according to the Bragg equation, $D=\lambda/2\sin\theta$). These results suggest that the S was successfully incorporated into the $K_2Ta_2O_6$. While the lattice spacing will increase if the S was doped into the $K_2Ta_2O_6$ at the state of S^{2-} (S^{2-} replace the sites of O^{2-}). Therefore, We speculate that the S as the S^{6+} species was introduced into the lattice sites of Ta^{5+} because the radius of S^{6+}(0.29nm) is smaller than the Ta^{5+}(0.64nm), which was responded to the diminish of lattice spacing in the samples x%S-KTO (x=5, 10, 15) compared to the pure $K_2Ta_2O_6$[6].

The SEM images of 0%S-KTO and 15%S-KTO are shown in the Fig2.(a) and (b). Both of the two samples are well-crystallized octahedral phase, manifesting the average size of 200-300nm with exposed facts of (111) face. It is the typical morphology for hydrothermal synthesized $K_2Ta_2O_6$, where the nuclei can grow freely in aqueous solution to form nanocrystals according to their natural crystallographic growth habits. Moreover, it is clearly that the morphology of $K_2Ta_2O_6$ was not obvious vibration with the added S source.

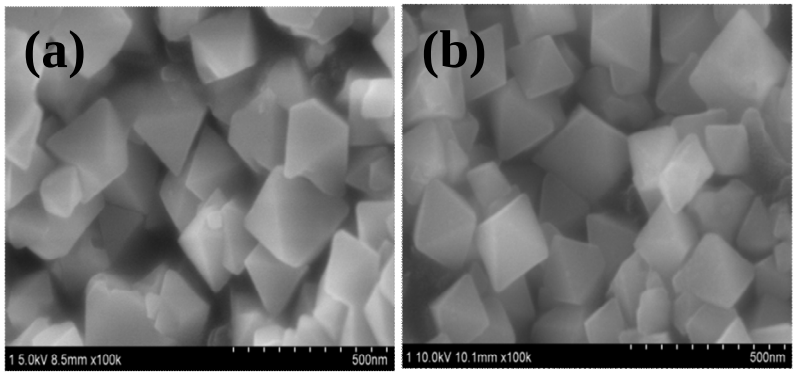

Fig2. SEM images of (a) 0%S-KTO and (b) 15%S-KTO.

The obtained samples are only response to the UV light and the sharp absorption edge demonstrate a slight red shift, as shown in the Fig3.a. And the corresponded calculated plots of$(ahv)^2$ against hv are shown in the Fig4.b. The band gap of samples calculated from the Fig3.b is 4.605eV for 0%S-KTO, 4.567eV for 5%S-KTO, 4.522eV for 10%S-KTO, 4.445eV for 15%S-KTO. It suggest that the band gap of obtained samples is red shift with the increase of S dopants.

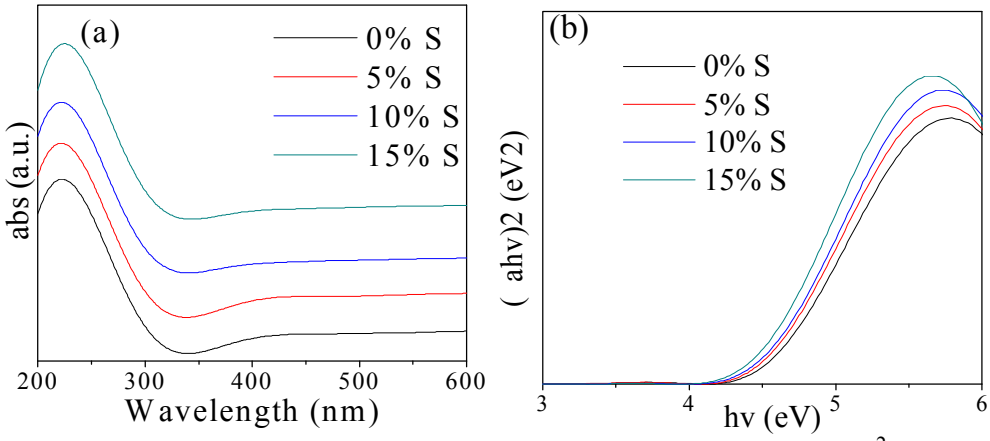

Fig3. (a) The UV-DRS spectrums of obtained samples and (b) Plots of $(\alpha hv)^2$ against hv for a direct transition.

The photocatalytic activity of x%S-KTO (x=0,5,10,15) were evaluated by aqueous degradation of RhB($1*10^{-5}$M) and MO (15mg/L) under UV irradiation. The degradation efficiency was determined by C/C_0, where C was the observed absorbance value of resultant solution at a certain irradiation time, C_0 was the absorbance value of the solution at the adsorption/desorption equilibrium.

As shown in Fig4(a), the aqeous solution of RhB is decomposed by x%S-KTO (x=0,5,10,15) about 12min. The degradation efficiency of RhB is slightly promoted with the increase of S doping amount. But the degradation efficency of S-KTO is prior to the pure $K_2Ta_2O_6$ in the decolorazition of MO under UV-light, as shown in the Fig4.(b). The highest degradation efficency was improved by 20% for the 10%S-KTO. The band gap is a key factor in the photocatalytic acitvity. The band gap of 5%S-KTO is wider than the 10%S-KTO, indicating that the excited electron in the vanlance band was hard to transfer to the conduction band, which results the low degradation effiency. However, although the 15%S-KTO is narrower than the 10%S-KTO, the degradation efficency is below than the 10%S-KTO, which was ascribed to the vacancy produced from the excess S dopants served as the center of elctrons and holes recombination. It is concluded that the S dopants exist the appropriate amount.

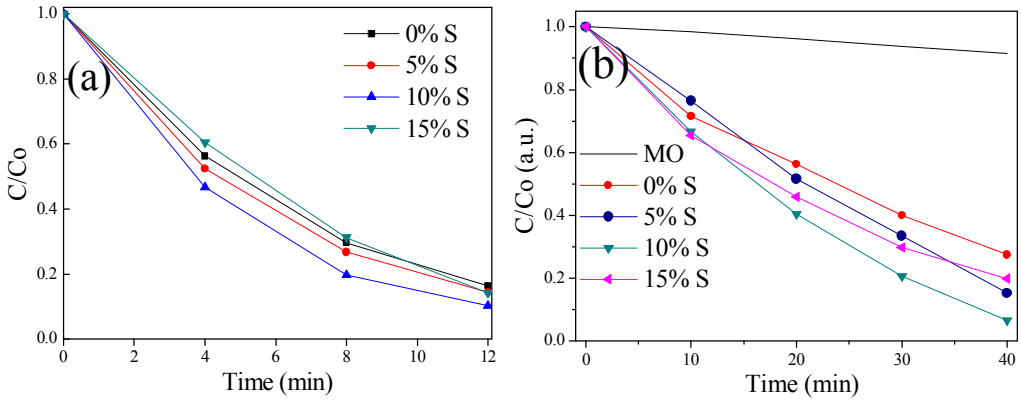

Fig 4.The degradation of (a) MO and (b) RhB under UV-irradiation using the x%S-KTO (x=0,5,10,15)

Conclusion

The samples of x%S-KTO(x=0,5,10,15) were fabricated via one step hydrothermal method. The XRD spectrum showed that the S was successfully doped into the $K_2Ta_2O_6$. During the photocatalytic process, the doped samples as prepared exhibited higher photocatalytic activity than pure $K_2Ta_2O_6$ on the degradation of MO and RhB under UV-light illumination. The 10%S-KTO presented the highest degradation activity in the decomposing of MO, RhB, suggesting that the S dopants have a appropriate amount. Here, we provided a way to enhance the photocatalytic activity of $K_2Ta_2O_6$ via nonmetal doping. However, there are further work for the perfect catalytic performance of $K_2Ta_2O_6$, which was a promising material for the removal of pollutants and separation of water.

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