

Characterization and photocatalytic activity of Cu-doped $K_2Nb_4O_{11}$

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Abstract

The Cu-doped tungsten bronze (TB) type potassium niobate $K_2Nb_4O_{11}$ was synthesized by solid-state reaction method in air. The crystal structure and morphology of the prepared samples were confirmed by X-ray diffraction analysis and scanning electron microscope. The photocatalytic activity of the prepared samples was evaluated using acid red G as a model organic compound and the photocatalytic reaction belongs to the first order kinetics. The results show that Cu-doping significantly increased the photocatalytic activity of $K_2Nb_4O_{11}$ catalyst when the concentration of Cu-doped was lower, but the photocatalytic activity of the catalyst was decreased when the concentration of Cu-doped was higher. Although the surface areas of the 0.2 wt.% Cu-doped $K_2Nb_4O_{11}$ and the 0.5 wt.% Cu-doped $K_2Nb_4O_{11}$ are very lower, the photocatalytic activities of these compounds are close to that of TiO_2 -P25. Copper doping is good for the compounds to form tetragonal TB structure and improving the crystallinity of the compounds. The diffuse reflectance spectrum of Cu-doped $K_2Nb_4O_{11}$ showed a red shift. X-ray photoelectron spectroscopy analysis confirmed that the niobium with mixed valence state exists in the crystal structure of the compound $K_2Nb_4O_{11}$. The effects of the Cu-doped and the mixed valence state of niobium on the photocatalytic activity of the catalyst were discussed.

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1. Introduction

The textile industry produces large quantities of highly colored effluents. Various chemical and physical processes were applied for color removal from textile effluents. One difficulty with these methods, is that they are not destructive but only transfer the contamination from one phase to another, therefore, a new and different kind of pollution is faced which calls for further treatment [1–4]. Recently, semiconductor photocatalysis that costs less money and does not create secondary contamination has become one of the most important technologies for the degradation of organic contaminants in water. Most of the research on semiconductor photocatalysts were focused on TiO_2 , which is known as one of the most effective photocatalysts for the degradation of organic pollutants, but its photocatalytic activity is influenced by a wide variety of factors such as, specific surface area, the adsorption affinity and capacity for organic contami-

nant, electron–hole recombination processes in the bulk and so on [5,6].

In the past two decades, many attentions have been paid for finding more efficient photocatalysts. A variety of niobates had been extensively studied as a new class of photocatalysts in the field of water splitting. Zou et al. [7] reported three photocatalysts Bi_2MnNbO_7 ($M = Al^{3+}$, Ga^{3+} and In^{3+}); $InMO_4$ ($M = Nb^{5+}$ and Ta^{5+}) and $BiMO_4$ ($M = Nb^{5+}$ and Ta^{5+}), which could split water into H_2 and/or O_2 under ultra-violet irradiation or visible light ($\lambda > 420$ nm). The photocatalytic activity increases significantly by loading co-catalysts on the surface of the photocatalyst, such as NiO and Pt. Kato and Kudo [8] studied on the photophysical and photocatalytic properties of layered perovskite $Sr_2(Ta_{1-x}Nb_x)_2O_7$. The results showed that the conduction band level of the $Sr_2(Ta_{1-x}Nb_x)_2O_7$ solid solution can be controlled by changing the ratio of niobium to tantalum. The $Sr_2(Ta_{1-x}Nb_x)_2O_7$ solid solution photocatalysts loaded with NiO co-catalysts decomposed water into H_2 and O_2 in a stoichiometric ratio. Domen and Ikeda [9] reported the photocatalytic activities of small particles (0.1–2 μm) of $K_4Nb_6O_{17}$ in water splitting and showed the photocatalytic activity for an overall

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decomposition of water of the Ni-loaded $K_4Nb_6O_{17}$ was twice as high as that for the original catalyst.

These researches described as above were mainly focused on the study of the photocatalytic properties of layered niobates in the field of water splitting. In this paper, we report another new type niobate $K_2Nb_4O_{11}$ used as the photocatalytic degradation dyes, which assumes a tetragonal tungsten bronze (TB) with space group $P4/mbm$ (127), and its molecular formula can be written as $K_{5.75}Nb_{10.85}O_{30}$ according to its crystal structure characteristic. The crystal structure of $K_2Nb_4O_{11}$ is constructed by NbO_6 octahedra, which form some triangle, quadrilateral and pentagonal tunnels. The pentagonal and quadrilateral tunnels are occupied by K cations, the triangle tunnels are occupied by Nb cations, and the tunnels make for better import of metal ions [10–12]. Up to now, there are many studies reported on the structures and properties of TB niobates, however, the study of the photocatalytic property of TB niobates in the field of photodegrading the pollution has hardly been reported. It is known that transition metal ions doped into catalysts can increase the quantum efficiency of the heterogeneous photocatalytic property by acting as electron (or hole) traps and by altering the e^-/h^+ pair recombination rate [13]. Copper is a kind of better dopant, Zhang et al. [14] studied copper-doped titanium oxide film. Their results showed copper doping improved the photocatalytic of the film. In this paper, we synthesized the TB potassium niobate $K_2Nb_4O_{11}$ and transition copper ions doped $K_2Nb_4O_{11}$ by solid-state reaction in air. So we would like to discuss the photocatalytic activity of the Cu-doped $K_2Nb_4O_{11}$, and investigate the influence of Cu-doped and the mixed valence state of niobium on the photocatalytic property of these compounds for photodegradation of acid red G.

2. Experimental

2.1. Sample preparation and characterization

The samples of $K_2Nb_4O_{11}$ were prepared by solid state-reaction method. Analytical grade of K_2CO_3 , Nb_2O_5 were used as starting materials. The stoichiometric amount of precursors were mixed and pressed into small pellets with an agate mortar. The small pellets were sintered in a crucible at $1000^\circ C$ for 2 h, and then cooled to room temperature. The samples for XRD analysis and experiments were prepared by manually grinding the bulk materials to powder with an agate mortar again.

The samples of Cu-doped potassium niobate were also prepared by solid-state reaction; the mixtures of K_2CO_3 , Nb_2O_5 , and $CuSO_4 \cdot 5H_2O$ were sintered at the same condition.

The structures of the $K_2Nb_4O_{11}$ crystal and Cu-doped $K_2Nb_4O_{11}$ were determined by X-ray diffraction (XRD). X-ray powder diffraction analyses of prepared samples were carried out on a Rigaku D/MAX-RB powder X-ray diffractometer. Scanning electron microscopy (SEM) was performed on JSM-5610LV scanning electron microscope. Surface areas were determined using nitrogen as the sorbate at 77 K in a static volumetric apparatus (Micromeritics ASAP 2010 sorptometer). The samples were previously outgassed at $180^\circ C$ for 16 h under

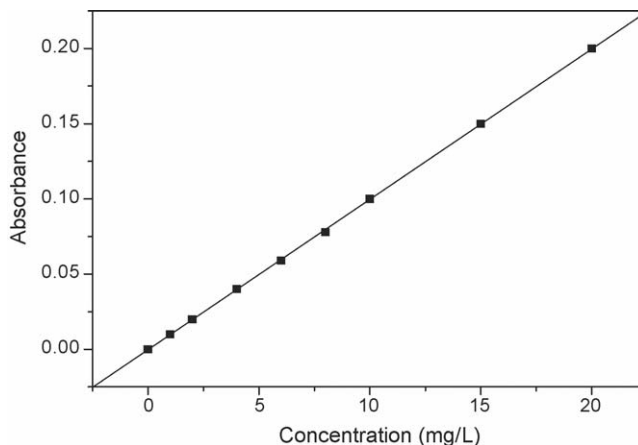


Fig. 1. Standard curve of acid red G at 505 nm (equation: $A = 0.01C - 0.0003 \approx 0.01C$, $R = 0.9999$).

a vacuum of 6.6×10^9 bar. The valence state of Nb was analyzed by X-ray photoelectron spectroscopy (XPS), using a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh-vacuum (UHV) chambers; the pressure in the chambers during the experiments was about 10^{-7} Pa. A Mg $K\alpha$ X-ray source was used. The analyzer was operated at 20 eV pass energy for high-resolution spectra and 50 eV for survey spectra. ESR study was conducted at room temperature with an ESP300E ESR spectrometer (Bruker) in X-band. g -Factor values were determined by comparison with an external standard (DPPH, $g = 2.0036$).

2.2. Photocatalytic experiments

The photodegradation of aqueous acid red G was carried out in a 500 ml beaker with constant magnetic stirring. A commercial 20 W UV lamp was used as the light source. Each as-prepared sample of 150 mg was suspended in 150 ml acid red G aqueous solution (30 mg/L). The distance between the liquid surface and the light source was about 8 cm. The light intensity was about 0.745 mW/cm^2 measured by using an UV-B radiometer. Sampled the solution six times in 2 h during the photocatalytic process, and the concentration of aqueous acid red G was determined by measuring the absorbance at 505 nm with an UV-vis spectrophotometer and a calibration curve (showed in Fig. 1). The photodegradation rate (X) is given by $X = (C_0 - C)/C_0 \approx (A_0 - A)/A_0$, where C_0 is initial concentration of acid red G, C the concentration at time t and A is the absorbance.

3. Result and discussion

3.1. XRD patterns analysis

X-ray powder diffraction patterns of prepared samples were shown in Fig. 2, the sharp peaks in the XRD patterns indicate a well crystallinity of the prepared samples when calcined at $1000^\circ C$ for 2 h. The result of XRD patterns confirmed that the compound $K_2Nb_4O_{11}$ assumes a tetragonal tungsten bronze

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