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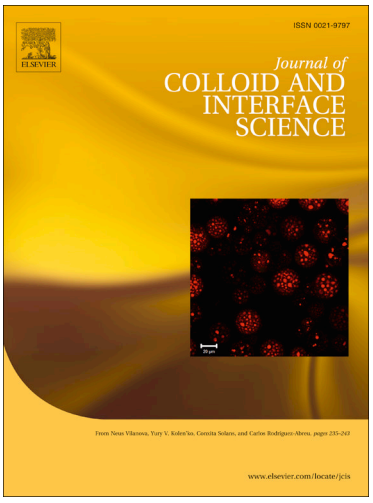

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Nanoheterostructures of potassium tantalate and nickel oxide for photocatalytic reduction of carbon dioxide to methanol in isopropanol

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ABSTRACT

Cubic perovskite-type and octahedral pyrochlore-type powders of potassium tantalate ($KTaO_3$) were selectively synthesized by a single-step hydrothermal method under different concentrations of potassium hydroxide (KOH). The obtained photocatalysts were characterized by X–ray diffraction (XRD), energy dispersive X-ray spectra (EDS), scanning electron microscopy (SEM), high–resolution transmission electron microscopy (HRTEM), and UV–vis absorption spectra (UV–vis). The photocatalytic activities of the $KTaO_3$ samples for reduction of carbon dioxide to methanol under UV light irradiation were investigated. The results showed that the KOH concentration played a significant role in determining the phases of the resultant products. Compared with the cubic crystalline structure, the octahedral crystalline structure exhibited the higher photocatalytic activity. In addition, the photocatalytic activities of $KTaO_3$ were obviously increased when a small amount of nickel oxide (NiO) was loaded as a co-catalyst. The highest rate of methanol formation was 1815 μmol/g/h when 2 wt% of NiO was loaded.

Keywords: photocatalytic reduction, CO_2, perovskite, pyrochlore, potassium tantalate, methanol

1. Introduction

In the past decades, studies toward promising clean and renewable energy have attracted broad attention to overcome environmental problems related to the rapidly increasing carbon dioxide (CO_2) emissions in the global atmosphere. Many research efforts have been devoted to reduce the emission of CO_2, which was mainly released from fossil fuel consumption. Photocatalytic CO_2 reduction is a promising method for converting it into useful organic fuels, such as methane [1], formaldehyde [2], methanol [3], and methyl formate [4].

After Inoue.et al [5]. first discovered the photocatalytic reduction of CO_2 to formaldehyde, methanol, formic acid, and methane, various kinds of materials have been tested in photocatalytic reduction of CO_2. Significant efforts have been made to develop alkali tantalate as an efficient photocatalyst. Kato and Kudo [6] investigated alkali tantalate $MTaO_3$ (M=Li, Na, K) with a perovskite structure for water splitting into H_2 and O_2 under UV irradiation. Lin et al. prepared the monoclinic crystal structure of sodium tantalate via a sol–gel method, which showed the superior photoactivity for H_2 evolution [7]. Li and his co-workers investigated the effect of potassium tantalate nanoflakes on photocatalytic reduction of CO_2 using water as an electron donor [8]. Ewa Mijowska and his co-works synthesized lithium tantalate nanoparticles through an impregnation method for photocatalytic hydrogen generation [9]. Potassium tantalate, as an efficient photocatalyst, is currently gaining noticeable attention in hydrogen generation [10], decomposition of organic compounds [11], and reduction of CO_2 [12,13], because it possesses outstanding physicochemical properties such as dielectric, low density, nontoxic, and high chemical stability. Generally, $KTaO_3$ was synthesized by the solid-state reaction or the alkoxide method, in which heat treatment at 1000℃ or above was required [14,15]. A defect structure or the larger-sized particle was favourably formed by conventional methods, in which the particle size and morphology was hardly controlled, leading to a low photocatalytic activity.

To the best of our knowledge, there are few reports about the photocatalytic CO_2 reduction over potassium tantalates. In the present study, we have successfully synthesized potassium tantalates with pyrochlore ($K_2Ta_2O_6$) and perovskite ($KTaO_3$) crystal structures by a single-step hydrothermal method. NiO nanoparticles were loaded onto the potassium tantalates via an impregnation method, the obtained nanoheterostructures of potassium tantalate and nickel oxide exhibited enhanced photocatalytic activity. The effects of structure, size, and the morphologies of potassium tantalates on the photocatalytic reduction of CO_2 were systematically studied.

2. Experimental

2.1 Catalyst Synthesis

Tantalum oxide (Ta_2O_5, 99.99%) was purchased from Aladdin Industrial Corporation. Potassium hydroxide (KOH, 96%), isopropanol (C_3H_8O, 99.7%), and nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$, 99.7%) were purchased from Tianjin Guangfu Chemical Reagent Company. Sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$, 99.8%) was purchased from Tianjin Kewei Chemical Reagent Company. All chemicals used in the experiments were analytical grade and without any further purification. Pyrochlore and perovskite powders of potassium tantalates were synthesized by a modified single-step hydrothermal method (Scheme 1A) [16,17]. Typically, 0.442 g of Ta_2O_5 powder was added into 30 mL aqueous alkaline solution containing 1.68 g of KOH and 0.2 g of sodium dodecyl sulfonate. After the obtained mixture was stirred for 30 min at room temperature, it was heated to 180℃ for 12 hours in a 75 mL Teflon-lined autoclave. After cooling to room temperature naturally, the precipitates were collected by centrifugation from the mixture, washed with ethanol and de-ionized water three times, and then dried at 65 ℃ for 12 h for further characterization.

Nanoheterostructures of potassium tantalate and nickel oxide was prepared by an impregnation method (Scheme 1B). 0.1 g of $KTaO_3$ photocatalyst containing 1–5 wt% of $Ni(NO_3)_2{\cdot}6H_2O$ was dissolved in 3 mL de-ionized water and was stirred at 40℃

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