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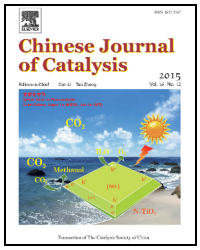

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Morphology-controlled synthesis and photocatalytic properties of $K_{1.9}Na_{0.1}Ta_2O_6{\cdot}2H_2O$

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ABSTRACT

The controllable synthesis of tantalate $K_{1.9}Na_{0.1}Ta_2O_6{\cdot}2H_2O$ has been successfully achieved by a two-step technique, namely, the molten salt and hydrothermal methods, at a low temperature. By simply varying the KOH concentration in the hydrothermal process, $K_{1.9}Na_{0.1}Ta_2O_6{\cdot}2H_2O$ particles with spherical, cuboctahedral, and durian-like morphologies were synthesized. The photocatalytic activity of the obtained samples for the degradation of rhodamine B was studied under ultraviolet light, which indicates that the photocatalytic properties of the samples are highly dependent on their morphologies. The $K_{1.9}Na_{0.1}Ta_2O_6{\cdot}2H_2O$ nanospheres, with rough surfaces and the highest specific surface area, exhibit the best performance. The present work provides a unique approach for the controlled synthesis of tantalate photocatalysts, which are difficult to achieve through other synthetic approaches.

1. Introduction

Tantalates have attracted considerable interest owing to their attractive roles in optic, optoelectronic, and electronic applications [1]. Recently, tantalates have been extensively studied in view of their high photocatalytic activities for water splitting into H_2 and the degradation of toxic substances [2–9]. Particularly, the quantum yield of NiO/$NaTaO_3$:La was estimated to be 56% at 270 nm, which is the highest quantum yield ever reported for catalysts in pure water splitting [9]. However, the tantalates are usually synthesized by solid state methods at high temperatures of approximately 1000 °C and require long synthesis times [9–11]. Such requirements may result in large grain growth (thus reducing the surface areas), which leads to a decrease in the photocatalytic activity [12]. Another possible approach for the synthesis of tantalates is the use of simple solution-based methods, in which soluble tantalum (Ta) precursors are used as starting materials. An alkoxide of Ta has been adopted to prepare $LiTaO_3$; however, this precursor is expensive and its solution is extremely sensitive to moisture [13,14]. A polymerized complex method from $TaCl_5$ has been employed to prepare the $A_2Nb_xTa_{2-x}O_7$ solid solutions (A = Ba, Sr) [15]. However, this approach is complicated and usually involves poisonous organic solvents. Others have used similar solution-based processes to synthesize tantalates by converting Ta_2O_5 to a Ta-based solution, although Ta_2O_5 is hardly dis-

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solved by regular chemical routes. For example, HF acid (40%), which is strongly corrosive and toxic, has been used to dissolve Ta_2O_5, and soluble tantalic acids ($Ta_2O_5{\cdot}nH_2O$) have been prepared starting either from Ta_2O_5 or from metallic Ta by the $KHSO_4$–oxalic acid method [16]. Among these solution-based preparations, a high temperature is also usually necessary to obtain the final product. Therefore, it is highly desirable to develop a low-temperature route to synthesize tantalates from cheap, nontoxic starting materials for their further application. Nevertheless, so far, only a few types of tantalates, such as $ATaO_3$ (A = Li, Na, K) [2], $Sr_2Ta_2O_7$ [3], and $Ba_5Ta_4O_{15}$ [6], have been synthesized from Ta_2O_5 by a hydrothermal method under high concentrations of OH^-, and the obtained products often exhibit an irregular-shaped morphology with a broad size distribution. Despite some success in the preparation of tantalates, it remains a major challenge to synthesize high-quality powder tantalates [17].

Morphology control of tantalates is another potentially important issue to meet different scientific and technological needs because of the strong correlation between the morphology and the physical or chemical properties. However, to the best our knowledge, it is still difficult to achieve morphology-controlled synthesis of tantalates. It is even more of a challenge to achieve morphology-controlled synthesis of tantalates from Ta_2O_5 at a relatively low temperature. Herein, using Ta_2O_5 as a starting material, we report on the facile synthesis of $K_{1.9}Na_{0.1}Ta_2O_6{\cdot}2H_2O$ (KNTO) crystals with controllable morphologies by a two-step synthesis technique, namely, the molten salt in combination with the hydrothermal method. Importantly, the morphology control of KNTO is achieved by simply adjusting the concentrations of KOH addition in the hydrothermal reaction. Taking an example, KNTO nanospheres were found to exhibit a distinguished photocatalytic activity for degrading rhodamine B (RhB) under ultraviolet (UV)-light irradiation.

2. Experimental

2.1. Sample preparation

$K_{1.9}Na_{0.1}Ta_2O_6{\cdot}2H_2O$ (KNTO) was synthesized by a two-step technique as published previously [4,5], namely, the molten salt and hydrothermal methods. Ta_2O_5 was converted to a soluble Ta precursor at 240 °C in the KOH/NaOH melt. The aqueous solution of the obtained Ta precursor is then transferred as a starting source of Ta to synthesize KNTO by the hydrothermal process at 180 °C. Table 1 lists the experimental details for the KNTO crystals with different morphologies, which are defined as samples 1–4. In a typical synthesis (sample 1 in Table 1), a mixture of Ta_2O_5 (0.5 g), NaOH (3.855 g), and KOH (5.651 g) was fused at 240 °C in a Teflon cup for 20 h and air-cooled to room temperature. Deionized water (50 mL) was then added into the cup to dissolve the alkalis. The solid collected after centrifugation was dissolved in deionized water (100 mL) with magnetic stirring. Then, 1.2 mL of 5 mol/L KOH aqueous solution (V_{KOH}) was added dropwise into a Teflon cup (50 mL) containing 33.8 mL (V_{Ta}) of the above clear solution under constant stirring at room temperature. With constant magnetic stirring for 8 h, the Teflon stainless autoclave was then maintained at 180 °C for 3 h and then air-cooled to room temperature. The samples obtained were collected by centrifugation, washed several times with deionized water, and air dried at 60 °C. Other products were prepared under the same conditions, except for the values of V_{Ta} and V_{KOH} (V_{Ta} + V_{KOH} = 35 mL).

Table 1
Composition and surface areas of the KNTO samples.

Sample	V_{Ta} (mL)	V_{KOH} (mL)	K:Na:Ta atomic ratio	Surface area (m^2/g)
1	33.8	1.2	1.83:0.09:2	7.86
2	33.0	2.0	1.85:0.09:2	2.58
3	31.8	3.2	1.88:0.08:2	0.89
4	27.0	8.0	1.91:0.08:2	0.65

2.2. Characterization

The samples were characterized by powder X-ray diffraction (XRD) on a Bruker D8 X-ray diffractometer with Cu K_α radiation, 0.02° step size, and 0.2 s step time. The compositions of the as-synthesized samples were determined by inductively coupled plasma emission spectrometry (ICP; Perkin-Elmer, Optima 5300 DV) after the sample was dissolved in a mixture of HNO_3 and HF solutions. Thermogravimetric (TG) characterization was performed on a NETZSCH STA 449F3 instrument. The sample was heated in an alumina crucible under air flow with a heating rate of 10 °C/min. Scanning electron microscope (SEM) images were collected on a field emission SEM (FESEM, ZEISS SUPRA55VP). Ultraviolet-visible (UV-vis) absorption spectra of the samples were recorded on a spectrophotometer (Shimadzu SolidSpec-3700DUV). Fourier transform infrared (FT-IR) spectra were obtained from a Perkin-Elmer 1600 FT-IR spectrometer with a KBr disk. The Brunauer-Emmett-Teller (BET) surface area was measured with a gas sorption instrument (Autosorb-iQ, Quantachrome Instruments).

2.3. Photocatalytic activity measurement

The photodegradation of RhB was carried out with 20 mg of powdered photocatalyst suspended in 100 mL of RhB solution (5 mg/L) at room temperature. An 8 W bactericidal lamp, with a maximum emission at 254 nm, was used as the light source. Prior to irradiation, the solution was first ultrasonicated for 5 min and then magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption-desorption equilibrium between the photocatalyst and RhB dye. During the photocatalytic progress, after each appropriate time, a 3-mL solution was sampled and centrifuged to remove the particles. The filtrate was analyzed by measuring the change of maximum absorption (553 nm) in the UV-vis spectrum (Shimadzu UV-1800).

3. Results and discussion

3.1. Crystal structure of the KNTO samples