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

Yingxuan Li ^{a,*}, Xiaoling Ding ^{a,b}, Jie Zhao ^a, Yunqing Zhu ^a, Yan Li ^{a,b}, Wenye Deng ^a, Chuanyi Wang ^{a,#}^a Laboratory of Environmental Sciences and Technology, Xinjiang Technical Institute of Physics & Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi 830011, Xinjiang, China^b University of Chinese Academy of Sciences, Beijing 100049, China

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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.

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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-

* Corresponding author. Tel: +86-991-3835879; Fax: +86-991-3838957; E-mail: yxli@ms.xjb.ac.cn

Corresponding author. Tel: +86-991-3835879; Fax: +86-991-3838957; E-mail: cywang@ms.xjb.ac.cn

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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 tantalum acids ($\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) 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 ($A = \text{Li, Na, K}$) [2], $\text{Sr}_2\text{Ta}_2\text{O}_7$ [3], and $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ [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 of 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 $\text{K}_{1.9}\text{Na}_{0.1}\text{Ta}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ (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

$\text{K}_{1.9}\text{Na}_{0.1}\text{Ta}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ (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

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

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} ($V_{\text{Ta}} + V_{\text{KOH}} = 35 \text{ mL}$).

2.2. Characterization

The samples were characterized by powder X-ray diffraction (XRD) on a Bruker D8 X-ray diffractometer with $\text{Cu K}\alpha$ 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

XRD patterns of the hydrothermally derived samples in the presence of different KOH concentrations (Table 1) are shown in Fig. 1(a). The XRD patterns were assigned to the pyrochlore structure with space group $Fd3m$ [18], indicating that these compounds consist of a single phase. As shown in Table 1, the ICP analysis indicates that the atomic ratios of K:Na:Ta in the samples are close to 1.9:0.1:2. TG analysis of all prepared samples showed a total weight loss of 6.1%–6.9% between room temperature and 600 °C for the products (Fig. 1(b)). The TG curves are in agreement with the previous reports and the weight loss can be attributed to loss of water [18,19]. Based on the TG and ICP analysis, the chemical formula of the samples prepared in different KOH concentrations was determined as $K_{1.9}Na_{0.1}Ta_2O_6 \cdot 2H_2O$ (KNTO) for concision. The FT-IR spectra of the obtained samples recorded in the range 400–4000 cm^{-1} are shown in Fig. 1(c). The broad band around 3300 cm^{-1} is normally ascribed to the O–H stretching vibrations of water molecules in the crystal structure. FT-IR peaks appearing around 1720 cm^{-1} can be assigned to the bending vibration of water. The FT-IR results are consistent with a previous report [19].

3.2. Morphologies of KNTO particles

In our synthetic process, KNTO particles with various sizes and shapes are achieved under different KOH concentrations in the hydrothermal process. Fig. 2 shows the FESEM images of the KNTO synthesized by varying the volume of 5 mol/L KOH used from 1.2 to 2.0, 3.2, and 8.0 mL. It can be seen that the KNTO products are composed of a large quantity of monodispersed particles. As shown in Fig. 2(a), nanospheres with good uniformity of shape were obtained when 1.2 mL of 5 mol/L KOH was added under hydrothermal conditions. The diameter of the nanospheres was approximately 150 nm. As shown in the inset of Fig. 2(a), the nanosphere was assembled by many tiny particles of diverse sizes, which resulted in a relatively rough surface of the spheres. When the volume of KOH solution was increased to 2.0 mL, spheres with a diameter from approximately 200 nm to 2.5 μm were produced, as shown in Fig. 2(b). The magnified view clearly indicates that the surfaces of the spheres were very smooth. Upon increasing the volume of

Fig. 2. SEM images of KNTO synthesized with various morphologies. (a) Nanospheres; (b) Microspheres; (c) Cuboctahedra; (d) Durian-like morphology. The insets are magnified individual microstructures.

the aqueous KOH solution from 2.0 to 3.2 mL, the morphology of the KNTO sample changed from spherical to cuboctahedral (or truncated octahedral) with an edge length from approximately 3 to 4 μm (Fig. 2(c)). The FESEM image in the inset of Fig. 2(c) also reveals that the vertices of the cuboctahedron are not perfectly flat, but are gently upward-curving. These features distinguish them from the typical cuboctahedral structure with flat faces. More interestingly, in the presence of 8.0 mL aqueous KOH, a durian-like morphology with numerous pyramid vertices was obtained, as shown in Fig. 2(d), which proves that this simple approach can enable the acquisition of unusual complex microstructural features. The broad size distribution shown in Fig. 2 might be caused by the quick nucleation of the KNTO under hydrothermal conditions [20].

First, the soluble $(K,Na)_8Ta_6O_{19} \cdot mH_2O$ was obtained by pre-treatment of the Ta_2O_5 in hydroxide melts [4,5]. When the concentration of K^+ reached or exceeded supersaturation, KNTO nuclei were formed under hydrothermal conditions, which served as seeds for subsequent growth into larger particles [6]. As reported, the chemical potential of the reaction system, as a

Fig. 1. XRD patterns (a), TG curves (b), and FT-IR spectra (c) of KNTO synthesized under different volumes of KOH added in the hydrothermal reaction.

driving force for the crystal growth, is mainly determined by the concentration of KOH [20]. Theoretically, the KOH quantities can cause the transformation of the KNT0 morphology, which is consistent with the observations from FESEM images. When $V_{\text{KOH}} = 1.2$ and 2.0 mL, the formation of the spheres followed the nucleation, growth, and aggregation processes in the hydrothermal condition, which has been discussed in detail previously [5]. The nonspherical structures shown in Fig. 2 result from the anisotropic growth rates of the crystal along the crystallographic directions. It is easy to determine that the cuboctahedra is bounded by eight (111) planes of the cubic lattice of KNT0. In our experiments, the formation of the cuboctahedral KNT0 arises from the slow growth rate of the (111) faces, which is induced by increasing the amount of KOH from 2.0 to 3.2 mL. From the observation of the KNT0 hierarchical structure in Fig. 2(d), it is presumed that this morphology can be considered to be generated by the interpenetrated growth of the octahedrons. According to a previous report [21], the geometrical shape of a crystal with cubic lattice is determined by the ratio (R) of the growth rate along the $\langle 100 \rangle$ versus $\langle 111 \rangle$ directions. A perfect octahedron will result when R is 1.73, and the cuboctahedra is formed when R is 0.87–1.73 [21].

3.3. Optical absorption of KNT0 particles

The UV-vis diffuse reflectance spectra of KNT0 synthesized under different conditions ($V_{\text{KOH}} = 1.2$ –8.0 mL) are shown in Fig. 3. It reveals that there is a small red shift of the absorption edge as the V_{KOH} used in the hydrothermal reactions is increased. The bandgaps of nanospheres, microspheres, cuboctahedral particles, and the durian-like sample are 4.88, 4.82, 4.77, and 4.73 eV, respectively. Generally, the electronic band structures are affected by the morphology, size, and defect of the photocatalysts [22]. The larger band gap energy of KNT0 synthesized under the condition of $V_{\text{KOH}} = 1.2$ mL might result from the small particle sizes. A similar phenomenon has been observed for the tantalite $\text{Sr}_2\text{Ta}_2\text{O}_7$ [3]. It can be seen from Fig. 2 that the sizes of the other three samples ($V_{\text{KOH}} = 2.0$ –8.0 mL) are all in the micrometer range. Therefore, for these three samples, the effect of particle size on the electronic structure can be

Fig. 3. UV-vis diffuse reflectance spectra of the KNT0 synthesized under different volumes of KOH added in the hydrothermal reaction.

neglected. The difference in the band gap energy is probably caused by the different surface atomic arrangement because each morphology possesses its own unique surface atomic arrangement [23].

3.4. Photocatalytic activity

The photocatalytic activities of the as-prepared catalysts with different morphologies are evaluated using RhB as the probe molecule under UV light irradiation. Fig. 4(a) shows the time profiles of C_t/C_0 under UV irradiation of KNT0 samples, where C_0 is the initial concentration of RhB at the absorption equilibrium of the photocatalyst before irradiation, and C_t is the corresponding concentration after irradiation for time t . As shown in Fig. 4(a), the nanospheres (synthesized at $V_{\text{KOH}} = 1.2$ mL) with the largest surface area ($7.86 \text{ m}^2/\text{g}$) exhibited the highest photoactivity for RhB photodegradation. The photoactivity of the samples decreased with the increasing V_{KOH} added in the hydrothermal process. The temporal evolution of the spectrum of RhB during the photodegradation over KNT0 nanospheres is shown in Fig. 4(b). It can be seen that the characteristic peak of RhB at 553 nm is gradually decreased with

Fig. 4. (a) Variation of RhB concentration during photocatalytic reaction with KNT0 samples; (b) Temporal absorption spectral changes of RhB in the presence of KNT0 nanospheres under UV light irradiation; (c) Repeated photocatalytic experiments of the KNT0 nanospheres.

Fig. 5. (a) XRD patterns of KNT0 nanospheres before (1) and after (2) photocatalytic reaction; (b) FESEM image of KNT0 nanospheres after photocatalytic reaction.

increasing photocatalytic reaction time. After 60 min of irradiation with UV light, RhB is almost completely degraded by the KNT0 nanospheres.

It is known that the activity of a photocatalyst is affected by many factors, including crystallinity, surface area, and active sites [5]. From Fig. 1(a), it can be seen that the sharp Bragg peaks of the four samples exhibit similar intensity, indicating that the crystallinity of the four samples is similar. Therefore, we can conclude that the different performance of the four samples is not as a result of crystallinity. As shown in Table 1, the surface area of the KNT0 samples decreases with the amount of KOH used in the hydrothermal process. This phenomenon is consistent with the consequence of the photocatalytic activity of the samples. The larger surface area can provide more active sites for the photocatalytic reaction, thus, the surface area may be the main factor that can contribute to the photocatalytic performance of the four samples. Moreover, as shown in Fig. 2(a), the KNT0 nanospheres with a rough surface are composed of many tiny particles of diverse sizes. As reported, the boundaries among the primary nanoparticles might be beneficial for the separation of photogenerated electron-hole pairs, which might be helpful for the enhancement of photocatalytic activity of the KNT0 nanospheres. Therefore, the KNT0 nanospheres show a significant advantage over the other three samples in RhB degradation. The stability of the KNT0 nanospheres in RhB degradation was also tested under the same reaction conditions. After complete degradation, the sample was separated by centrifugation and washed several times with deionized water and methanol. The recovered catalyst was used for the next experiment. Fig. 4(c) shows the results of RhB degradation for four runs. It suggests that no obvious decline in RhB degradation occurs after four cycling tests for the KNT0 nanospheres, indicating their excellent photostability. The XRD pattern and FESEM image of the sample after the reaction are shown in Fig. 5. No significant changes were found in the crystal structure and morphology of the used photocatalyst, confirming the stability of the photocatalyst.

4. Conclusions

A two-step synthetic method has been used for the con-

trolled synthesis of KNT0 at a low temperature. By fine tuning a single parameter, the amount of KOH added in the hydrothermal process, KNT0 with spherical, cuboctahedral, and duriar-like morphologies can be selectively prepared. Interestingly, the as-obtained crystals showed different photocatalytic performance, mainly depending on the morphology. The surface areas of the samples have been confirmed to be responsible for their final activity. This technique is expected to be applicable for the precise control of the shape of other tantalate materials that exhibit promising physicochemical properties.

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Graphical Abstract

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

Yingxuan Li*, Xiaoling Ding, Jie Zhao, Yunqing Zhu, Yan Li, Wenye Deng, Chuanyi Wang*

Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences; University of Chinese Academy of Sciences

A method has been developed for the morphology-controlled synthesis of $K_{1.9}Na_{0.1}Ta_2O_6 \cdot 2H_2O$ at low temperature, which results in the ability to tune the photocatalytic activity for RhB degradation with changing morphology.

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^a中国科学院新疆理化技术研究所环境科学与技术研究室, 中国科学院特殊环境功能材料与器件重点实验室, 新疆乌鲁木齐830011

^b中国科学院大学, 北京100049

摘要: 钽酸盐光催化材料往往具有较高的光催化活性。近年报道的钽酸盐光催化剂主要采用传统高温固相法制备, 该方法不可避免地导致高温烧结, 使合成的钽酸盐颗粒较大, 比表面积较小, 而且该方法具有不可克服的晶体转变、结晶度差、分解、挥发和纯度低等缺点, 使制备的光催化剂活性较低。而纳米材料由于粒径小, 提高了电子和空穴的扩散速度, 大大降低了电子和空穴在材料内的复合几率, 从而使光催化材料活性大幅提高。此外, 粒径减小也使表面原子迅速增多, 减小了光的漫反射, 同时也使光吸收不易达到饱和, 有利于提高光吸收效率。因此, 制备纳米材料是提高半导体光催化剂活性的有效手段。

目前, 采用湿化学的溶液合成方法能在较低温度下获得粒度小且均匀、计量比准确的光催化剂粉末, 但是合成钽酸盐光催化剂的水溶性钽前体即乙醇钽(或氯化钽)价格昂贵, 而且对潮湿极端敏感易水解, 使产物纯度降低, 不适合工业化生产。近年来, 尽管有文献报道以 Ta_2O_5 为原料利用水热、溶胶-凝胶和共沉淀等方法制备钽酸盐, 但其合成条件苛刻, 合成步骤复杂, 合成周期较长, 耗能大, 产物产量较低且不均匀, 很难实现产物的形貌控制来筛选出适合光催化反应的材料。目前关于纳米钽酸盐光催化材料形貌控制方面的研究鲜有报道, 主要是由于 Ta_2O_5 极难溶解, 很难实现液相合成。因此, 纳米钽酸盐光催化材料的可控制备是研究的难点。

我们发展了熔盐-水热制备钽酸盐新方法, 实现了 $K_{1.9}Na_{0.1}Ta_2O_6 \cdot 2H_2O$ 的可控制备。利用熔盐法制备一种可溶性钽酸盐前驱体, 再通过水热法在液相进一步反应制得纳米钽酸盐光催化材料 $K_{1.9}Na_{0.1}Ta_2O_6 \cdot 2H_2O$, 通过控制反应条件实现了纳米钽酸盐 $K_{1.9}Na_{0.1}Ta_2O_6 \cdot 2H_2O$ 的形貌调控, 得到了纳米球、微球、去顶八面体形貌和类似榴莲形貌等不同形貌, 而利用其它制备方法很难控制钽酸盐的形貌。另外, 研究了制备材料吸附和光催化降解罗丹明B的性能, 发现该材料光催化活性与形貌直接相关。

表征结果表明, 制备样品的X射线衍射(XRD)谱图尖锐, 结晶较好, 其各衍射峰位置均与 $K_2Ta_2O_6$ 一致, 为纯相烧绿石结构, 属于立方晶系, 空间群为 $Fd3m$ 。通过分析合成材料的元素组成及含量, 确定K:Na:Ta比例近似为1.9:0.1:2。为了进一步研究属于烧绿石型化合物 $K_{1.9}Na_{0.1}Ta_2O_6 \cdot 2H_2O$ 的结构, 对不同形貌材料进行了红外光谱测试, 所有样品在450–1000 cm^{-1} 的谱峰可归属于(K,

Na)–O和Ta–O键的振动, 3300 cm^{-1} 左右为晶体结构中水的羟基伸缩振动峰, 1720 cm^{-1} 左右是晶体结构中水的弯曲振动峰. 可以看出, 不同形貌材料的红外谱图吸收带宽度和位置十分相似, 只存在小的偏移和变化, 进一步表明不同形貌的材料具有相似的晶体结构, 与XRD结果一致. 差热-热重分析确定了结构中所含结晶水数量近似为2. 光催化性能测试结果表明, 具有纳米球形貌的材料比表面积较大, 因而光催化活性最高.

关键词: 钽酸盐; $\text{K}_{1.9}\text{Na}_{0.1}\text{Ta}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$; 形貌可控合成; 水热法; 纳米球; 光催化

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*通讯联系人. 电话: (0991)3838879; 传真: (0991)3838957; 电子信箱: yxli@ms.xjb.ac.cn

#通讯联系人. 电话: (0991)3838879; 传真: (0991)3838957; 电子信箱: cywang@ms.xjb.ac.cn

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